

Chemistry



10th Edition

Whitten | Davis | Peck | Stanley

International Table of Atomic Weights (IUPAC 2009)

Based on relative atomic mass of ¹²C = 12.
The following values apply to elements as they exist in materials of terrestrial origin and to certain artificial elements.
Values in parentheses are the mass number of the isotope of longest half-life.

Name	Symbol	Atomic Number	Atomic Weight	Name	Symbol	Atomic Number	Atomic Weight	Name	Symbol	Atomic Number	Atomic Weight
Actinium ^{d,e}	Ac	89	(227)	Hafnium	Hf	72	178.49	Radium ^{d,e,g}	Ra	88	(226)
Aluminum ^a	Al	13	26.9815386	Hassium ^{d,e}	Hs	108	(277)	Radon ^{d,e}	Rn	86	(222)
Americium ^{d,e}	Am	95	(243)	Helium ^g	He	2	4.002602	Rhenium	Re	75	186.207
Antimony	Sb	51	121.760	Holmium ^a	Ho	67	164.93032	Rhodium ^a	Rh	45	102.90550
(Stibium)				Hydrogen ^{b,c,g}	H	1	1.008	Roentgenium ^{d,e}	Rg	111	(280)
Argon ^{b,g}	Ar	18	39.948	Indium	In	49	114.818	Rubidium ^g	Rb	37	85.4678
Arsenic ^a	As	33	74.92160	Iodine ^a	I	53	126.90447	Ruthenium ^g	Ru	44	101.07
Astatine ^{a,d}	At	85	(210)	Iridium	Ir	77	192.217	Rutherfordium ^{d,e}	Rf	104	(265)
Barium	Ba	56	137.327	Iron	Fe	26	55.845	Samarium ^g	Sm	62	150.36
Berkelium ^{d,e}	Bk	97	(247)	Krypton ^{c,g}	Kr	36	83.798	Scandium ^a	Sc	21	44.955912
Beryllium ^a	Be	4	9.012182	Lanthanum ^g	La	57	138.90547	Seaborgium ^{d,e}	Sg	106	(271)
Bismuth ^a	Bi	83	208.98040	Lawrencium ^{d,e}	Lr	103	(262)	Selenium	Se	34	78.96
Bohrium ^{d,e}	Bh	107	(270)	Lead ^{b,g}	Pb	82	207.2	Silicon ^{b,c}	Si	14	28.085
Boron ^{b,c,g}	B	5	10.81	Lithium ^{b,c,g}	Li	3	6.94	Silver ^g	Ag	47	107.8682
Bromine	Br	35	79.904	Livermorium ^{d,e}	Lv	116	(293)	Sodium	Na	11	22.98976928
Cadmium	Cd	48	112.411	Lutetium ^g	Lu	71	174.9668	(Natrium) ^a			
Calcium ^g	Ca	20	40.078	Magnesium	Mg	12	24.3050	Strontium ^{b,g}	Sr	38	87.62
Californium ^{d,e}	Cf	98	(251)	Manganese ^a	Mn	25	54.938045	Sulfur ^{b,c}	S	16	32.06
Carbon ^{c,g}	C	6	12.011	Meitnerium ^{d,e}	Mt	109	(276)	Tantalum	Ta	73	180.94788
Cerium ^{b,g}	Ce	58	140.116	Mendelevium ^{d,e}	Md	101	(258)	Technetium ^{d,e}	Tc	43	(98)
Cesium ^a	Cs	55	132.9054519	Mercury	Hg	80	200.59	Tellurium ^g	Te	52	127.60
Chlorine ^c	Cl	17	35.45	Molybdenum ^{b,g}	Mo	42	95.96	Terbium ^a	Tb	65	158.92535
Chromium	Cr	24	51.9961	Neodymium ^g	Nd	60	144.242	Thallium ^c	Tl	81	204.38
Cobalt ^a	Co	27	58.933195	Neon ^{c,g}	Ne	10	20.1797	Thorium ^{b,f,g}	Th	90	232.038106
Copernicium ^{d,e}	Cn	112	(285)	Neptunium ^{d,e}	Np	93	(237)	Thulium ^{a,b}	Tm	69	168.93421
Copper	Cu	29	63.546	Nickel	Ni	28	58.6934	Tin ^g	Sn	50	118.710
Curium ^{d,e}	Cm	96	(247)	Niobium ^a	Nb	41	92.90638	Titanium	Ti	22	47.867
Darmstadtium ^{d,e}	Ds	110	(281)	Nitrogen ^{b,c,g}	N	7	14.007	Tungsten	W	74	183.84
Dubnium ^{d,e}	Db	105	(268)	Nobelium ^{d,e}	No	102	(259)	(Wolfram)			
Dysprosium ^{c,g}	Dy	66	162.50	Osmium ^g	Os	76	190.23	Ununoctium ^{d,e}	Uuo	118	(294)
Einsteinium ^{d,e}	Es	99	(252)	Oxygen ^{b,c,g}	O	8	15.999	Ununpentium ^{d,e}	Uup	115	(288)
Erbium ^g	Er	68	167.259	Palladium ^g	Pd	46	106.42	Ununseptium ^{d,e}	Uus	117	(294)
Europium ^g	Eu	63	151.964	Phosphorus ^a	P	15	30.973762	Ununtrium ^{d,e}	Uut	113	(284)
Fermium ^{d,e}	Fm	100	(257)	Platinum	Pt	78	195.084	Uranium ^{c,f,g}	U	92	238.02891
Flerovium ^{d,e}	Fl	114	(289)	Plutonium ^{d,e}	Pu	94	(244)	Vanadium	V	23	50.9415
Fluorine ^a	F	9	18.9984032	Polonium ^{d,e}	Po	84	(209)	Xenon ^{a,c,g}	Xe	54	131.293
Francium ^d	Fr	87	(223)	Potassium	K	19	39.0983	Ytterbium ^g	Yb	70	173.054
Gadolinium ^g	Gd	64	157.25	(Kalium)				Yttrium ^a	Y	39	88.90585
Gallium	Ga	31	69.723	Praseodymium ^a	Pr	59	140.90765	Zinc	Zn	30	65.38
Germanium	Ge	32	72.63	Promethium ^{d,e}	Pm	61	(145)	Zirconium ^g	Zr	40	91.224
Gold ^a	Au	79	196.966569	Protactinium ^f	Pa	91	231.03588				

^aElements with only one stable nuclide.

^bElement for which known variation in isotopic abundance in terrestrial samples limits the precision of the atomic weight given.

^cElement for which users are cautioned against the possibility of large variations in atomic weight due to inadvertent or undisclosed artificial separation in commercially available materials.

^dElement has no stable nuclides. The value enclosed in parentheses indicates the mass of the longest-lived isotope of the element.

^eRadioactive element that lacks a characteristic terrestrial isotopic composition.

^fAn element, without stable nuclide(s), exhibiting a range of characteristic terrestrial compositions of long-lived radionuclide(s) such that a meaningful atomic weight can be given.

^gIn some geological specimens this element has an anomalous isotopic composition, corresponding to an atomic weight significantly different from that given.

Copyright 2013 Cengage Learning. All Rights Reserved. May not be copied, scanned, or duplicated, in whole or in part. Due to electronic rights, some third party content may be suppressed from the eBook and/or eChapter(s). Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. Cengage Learning reserves the right to remove additional content at any time if subsequent rights restrictions require it.

Note: Atomic masses are IUPAC values (2009, up to four decimal places). More accurate values for some elements are given in the International Table of Atomic Weights on the facing page.

Location of Commonly Used Information

Atomic and Molecular Properties

Atomic and ionic radii	178, 184
Aufbau order, Aufbau Principle	153–158
Bond energies	259–260, 568–571
Bond lengths	259–260
Electron affinities	182
Electron configurations	Appendix B
Electronegativity values	186
Electronic, molecular, and ionic geometries	321
Hund's Rule	155
Ionization energies	180
Molecular orbital diagrams	334, 337, 339–340
Pauli Exclusion Principle	154
Planck's equation	137
Quantum numbers (rules)	147

Thermodynamic Properties, Kinetics, Equilibrium, States of Matter

Absolute entropies	Appendix K
Arrhenius equation	643–647
Clausius–Clapeyron equation	467
Colligative properties (equations)	518, 524–525, 529, 531
Enthalpies of formation	Appendix K
Free energies of formation	Appendix K
Gas laws	418
Heats of vaporization, fusion	465, 470, Appendix E
Hess's Law	564–568
LeChatelier's Principle	679–686
Specific heats, heat capacities	Appendix E
van't Hoff equation	699
Vapor pressure of water	Appendix E

Acids, Bases, and Salts

Acid–base indicators	763–766
Amphoteric oxides, hydroxides	195, 355
Common strong acids and bases	210, 213, 710
Dissociation constants (complex ions), K_d	Appendix I
Ionization constants for weak acids, K_a	Appendix F
Ionization constants for weak bases, K_b	Appendix G
Names and formulas of common ions	219
Solubility product constants, K_{sp}	Appendix H
Solubility guidelines	213–215

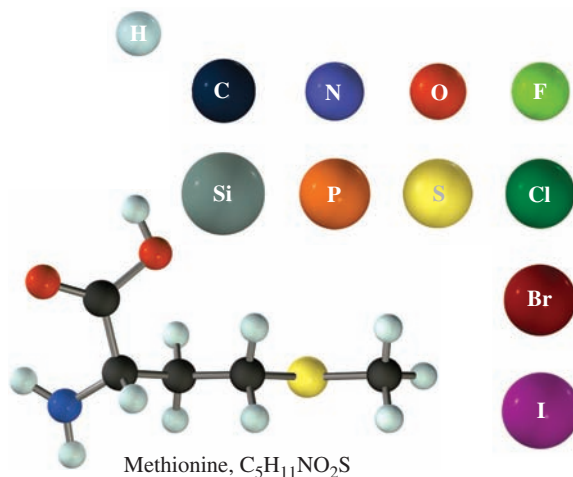
Electrochemistry

Activity series	229
Faraday's Law	808–809
Nernst equation	820, 827–828
Standard reduction potentials, E^0	Appendix J

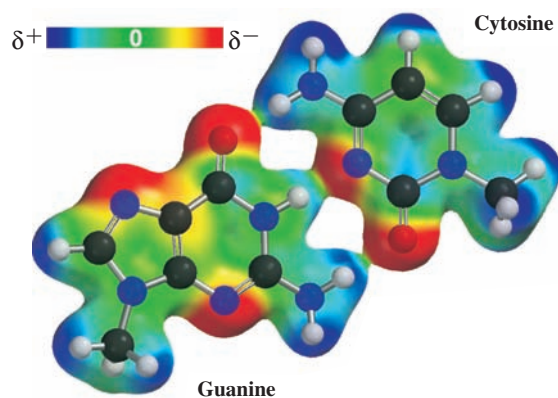
Miscellaneous

Classification of organic compounds	911, 931
Lewis formulas (rules)	261–274
Naming coordination compounds	995–997
Naming inorganic compounds	217–221
Naming organic compounds	893–906,
Organic functional groups	911–931
Oxidation states (common)	187–189

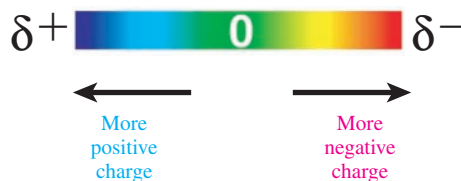
Element Colors for Models



Color Scale for Electrical Charge Potential (ECP) Surfaces



Hydrogen bonding between two DNA base pairs



Useful Constants (For a more complete list, see Appendix D)

Atomic mass unit	$1 \text{ amu} = 1.6605 \times 10^{-24} \text{ g}$
Avogadro's number	$N = 6.02214129 \times 10^{23} \text{ particles/mol}$
Electronic charge	$e = 1.60217656 \times 10^{-19} \text{ coulombs}$
Faraday constant	$F = 96,485 \text{ coulombs/equivalent}$ $= 96,485 \text{ coulombs/mol } e^{-}$
Gas constant	$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = 1.987 \frac{\text{cal}}{\text{mol} \cdot \text{K}}$ $= 8.3145 \frac{\text{J}}{\text{mol} \cdot \text{K}} = 8.3145 \frac{\text{kPa} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}}$
Ion product for water	$K_w = 1.0 \times 10^{-14}$
Pi	$\pi = 3.1416$
Planck's constant	$h = 6.62606957 \times 10^{-34} \text{ J} \cdot \text{s}$ $= 6.62606896 \times 10^{-27} \text{ erg} \cdot \text{s}$
Speed of light (in vacuum)	$c = 2.99792458 \times 10^8 \text{ m/s}$

Useful Relationships (For a more complete list, see Appendix C)

Mass and Weight SI Base Unit: Kilogram (kg) 1 kilogram = 1000 grams = 2.205 pounds 1 gram = 1000 milligrams 1 pound = 453.59 grams 1 amu = 1.6606×10^{-24} grams 1 gram = 6.022×10^{23} amu 1 ton = 2000 pounds	Length SI Base Unit: Meter (m) 1 inch = 2.54 centimeters (exactly) 1 meter = 100 centimeters = 39.37 inches 1 yard = 0.9144 meter 1 mile = 1.609 kilometers 1 kilometer = 1000 meters = 0.6215 mile 1 Ångstrom = 1.0×10^{-10} meters = 1.0×10^{-8} centimeters
Volume SI Base Unit: Cubic Meter (m³) 1 liter = 0.001 cubic meter 1 liter = 1000 cubic centimeters = 1000 mL 1 liter = 1.056 quarts 1 quart = 0.9463 liter 1 milliliter = 0.001 liter = 1 cubic centimeter 1 cubic foot = 7.475 gallons = 28.316 liters 1 gallon = 4 quarts	Energy SI Base Unit: Joule (J) 1 calorie = 4.184 joules = $4.129 \times 10^{-2} \text{ L} \cdot \text{atm}$ 1 joule = $1 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} = 0.23901 \text{ calorie}$ 1 joule = $1 \times 10^7 \text{ ergs}$ 1 electron volt = $1.6022 \times 10^{-19} \text{ joule}$ 1 electron volt = 96.485 kJ/mol 1 L · atm = 24.217 calories = 101.325 joules
Pressure SI Base Unit: Pascal (Pa) 1 pascal = $1 \frac{\text{kg}}{\text{m} \cdot \text{s}^2} = 1 \text{ newton/m}^2$ 1 atmosphere = 760 torr = 760 millimeters of mercury = 1.01325×10^5 pascals = 1.01325 bar = 14.70 pounds per square inch 1 torr = 1 millimeter of mercury	Temperature SI Base Unit: Kelvin (K) 0 K = -273.15°C $\underline{K} = ^\circ\text{C} + 273.15^\circ$ $\underline{^\circ\text{F}} = 1.8(^{\circ}\text{C}) + 32^\circ$ $\underline{^\circ\text{C}} = \frac{^\circ\text{F} - 32^\circ}{1.8}$

This is an electronic version of the print textbook. Due to electronic rights restrictions, some third party content may be suppressed. Editorial review has deemed that any suppressed content does not materially affect the overall learning experience. The publisher reserves the right to remove content from this title at any time if subsequent rights restrictions require it. For valuable information on pricing, previous editions, changes to current editions, and alternate formats, please visit www.cengage.com/highered to search by ISBN#, author, title, or keyword for materials in your areas of interest.

Chemistry

TENTH EDITION

KENNETH W. WHITTEN

University of Georgia, Athens

RAYMOND E. DAVIS

University of Texas at Austin

M. LARRY PECK

Texas A&M University

GEORGE G. STANLEY

Louisiana State University



Australia • Brazil • Japan • Korea • Mexico • Singapore • Spain • United Kingdom • United States

Chemistry, Tenth Edition**Kenneth W. Whitten, Raymond E. Davis,
M. Larry Peck, George G. Stanley**

Publisher: Mary Finch

Executive Editor: Lisa Lockwood

Developmental Editor: Alyssa White

Assistant Editor: Elizabeth Woods

Media Editor: Lisa Weber

Brand Manager: Nicole Hamm

Market Development Manager:
Janet del Mundo

Content Project Manager: Teresa L. Trego

Art Director: Maria Epes

Manufacturing Planner: Judy Inouye

Rights Acquisitions Specialist: Don Schlotman

Production Service: Graphic World Inc.

Photo Researcher: QBS Learning

Text Researcher: QBS Learning

Copy Editor: Graphic World Inc.

Illustrators: Graphic World Inc., Greg Gambino

Text Designer: RHDG Riezebos Holzbaur

Cover Designer: Bartay Studios

Cover Image: © Dale Wilson @Photographer's
Choice RF

Compositor: Graphic World Inc.

© 2014, 2010 Brooks/Cole, Cengage Learning

ALL RIGHTS RESERVED. No part of this work covered by the copyright herein may be reproduced, transmitted, stored, or used in any form or by any means, graphic, electronic, or mechanical, including but not limited to photocopying, recording, scanning, digitizing, taping, Web distribution, information networks, or information storage and retrieval systems, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without the prior written permission of the publisher.

For product information and technology assistance, contact us at
Cengage Learning Customer & Sales Support, 1-800-354-9706.

For permission to use material from this text or product,
submit all requests online at **www.cengage.com/permissions**.
Further permissions questions can be e-mailed to
permissionrequest@cengage.com.

Library of Congress Control Number: 2012950844

ISBN-13: 978-1-133-61066-3

ISBN-10: 1-133-61066-8

Brooks/Cole20 Davis Drive
Belmont, CA 94002-3098
USA

Cengage Learning is a leading provider of customized learning solutions with office locations around the globe, including Singapore, the United Kingdom, Australia, Mexico, Brazil, and Japan. Locate your local office at **www.cengage.com/global**.

Cengage Learning products are represented in Canada by
Nelson Education, Ltd.

To learn more about Brooks/Cole, visit **www.cengage.com/brookscole**

Purchase any of our products at your local college store or at our preferred online store **www.CengageBrain.com**.

Printed in the United States of America
1 2 3 4 5 6 7 17 16 15 14 13

.....

This edition of Chemistry is gratefully dedicated to Professor Emeritus Kenneth W. Whitten and the late Professor Kenneth D. Gailey, whose pedagogic insights and clarity of organization provided guidance for generations of students and laid the foundation for the many successful editions of this book.

RED, MLP, and GGS

Brief Contents

1	The Foundations of Chemistry	1
2	Chemical Formulas and Composition Stoichiometry	43
3	Chemical Equations and Reaction Stoichiometry	81
4	The Structure of Atoms	115
5	Chemical Periodicity	173
6	Some Types of Chemical Reactions	207
7	Chemical Bonding	249
8	Molecular Structure and Covalent Bonding Theories	287
9	Molecular Orbitals in Chemical Bonding	329
10	Reactions in Aqueous Solutions I: Acids, Bases, and Salts	347
11	Reactions in Aqueous Solutions II: Calculations	375
12	Gases and the Kinetic–Molecular Theory	401
13	Liquids and Solids	449
14	Solutions	505
15	Chemical Thermodynamics	551
16	Chemical Kinetics	611
17	Chemical Equilibrium	667
18	Ionic Equilibria I: Acids and Bases	709
19	Ionic Equilibria II: Buffers and Titration Curves	749
20	Ionic Equilibria III: The Solubility Product Principle	779

- 21** Electrochemistry 803
- 22** Nuclear Chemistry 851
- 23** Organic Chemistry I: Formulas, Names, and Properties 887
- 24** Organic Chemistry II: Shapes, Selected Reactions, and Biopolymers 953
- 25** Coordination Compounds 989
- 26** Metals I: Metallurgy 1017
- 27** Metals II: Properties and Reactions 1035
- 28** Some Nonmetals and Metalloids 1057

- APPENDIX A** Some Mathematical Operations A-1
- APPENDIX B** Electronic Configurations of the Atoms of the Elements A-9
- APPENDIX C** Common Units, Equivalences, and Conversation Factors A-12
- APPENDIX D** Physical Constants A-15
- APPENDIX E** Some Physical Constants for a Few Common Substances A-16
- APPENDIX F** Ionization Constants for Weak Acids at 25°C A-18
- APPENDIX G** Ionization Constants for Weak Bases at 25°C A-20
- APPENDIX H** Solubility Product Constants for Some Inorganic Compounds at 25°C A-21
- APPENDIX I** Dissociation Constants for Some Complex Ions A-23
- APPENDIX J** Standard Reduction Potentials in Aqueous Solution at 25°C A-24
- APPENDIX K** Selected Thermodynamic Values at 298.15 K A-27
- APPENDIX L** Answers to Selected Even-Numbered Numerical Exercises A-30

Index of Equations E-1

Glossary/Index I-1

Contents

About the Authors xv

For the Instructor xvi

For the Student xxviii

1 The Foundations of Chemistry 1

- 1-1 Matter and Energy 4
- 1-2 Chemistry—A Molecular View of Matter 5
- 1-3 States of Matter 9
- 1-4 Chemical and Physical Properties 10
- 1-5 Chemical and Physical Changes 12
- 1-6 Mixtures, Substances, Compounds, and Elements 13

CHEMISTRY IN USE: Names of the Elements 18

- 1-7 Measurements in Chemistry 19
- 1-8 Units of Measurement 20
- 1-9 The Unit Factor Method (Dimensional Analysis) 22
- 1-10 Percentage 26
- 1-11 Density and Specific Gravity 26
- 1-12 Heat and Temperature 29
- 1-13 Heat Transfer and the Measurement of Heat 31

Key Terms 35

Exercises 36

2 Chemical Formulas and Composition Stoichiometry 43

- 2-1 Chemical Formulas 44
- 2-2 Ions and Ionic Compounds 48
- 2-3 Names and Formulas of Some Ionic Compounds 49

2-4 Atomic Weights 51

2-5 The Mole 51

CHEMISTRY IN USE: Avogadro's Number 55

- 2-6 Formula Weights, Molecular Weights, and Moles 56
- 2-7 Percent Composition and Formulas of Compounds 60
- 2-8 Derivation of Formulas from Elemental Composition 61
- 2-9 Determination of Molecular Formulas 65
- 2-10 Some Other Interpretations of Chemical Formulas 67
- 2-11 Purity of Samples 71

Key Terms 72

Exercises 73

3 Chemical Equations and Reaction Stoichiometry 81

- 3-1 Chemical Equations 82
- 3-2 Calculations Based on Chemical Equations 88
- 3-3 The Limiting Reactant (Reagent) Concept 91
- 3-4 Percent Yields from Chemical Reactions 95
- 3-5 Sequential Reactions 96
- 3-6 Concentrations of Solutions 97
- 3-7 Dilution of Solutions 102
- 3-8 Using Solutions in Chemical Reactions 103

Key Terms 106

Exercises 106

4 The Structure of Atoms 115

SUBATOMIC PARTICLES 116

- 4-1 Fundamental Particles 116
- 4-2 The Discovery of Electrons 117
- 4-3 Canal Rays and Protons 119
- 4-4 Rutherford and the Nuclear Atom 120
- 4-5 Atomic Number 121
- 4-6 Neutrons 122
- 4-7 Mass Number and Isotopes 123
- 4-8 Mass Spectrometry and Isotopic Abundance 124
- 4-9 The Atomic Weight Scale and Atomic Weights 126

CHEMISTRY IN USE: Stable Isotope Ratio Analysis 127

- 4-10 The Periodic Table: Metals, Nonmetals, and Metalloids 129

THE ELECTRONIC STRUCTURES OF ATOMS 134

- 4-11 Electromagnetic Radiation 134
- 4-12 The Photoelectric Effect 138
- 4-13 Atomic Spectra and the Bohr Atom 138
 - ENRICHMENT: The Bohr Theory and the Balmer-Rydberg Equation** 141
- 4-14 The Wave Nature of the Electron 144
- 4-15 The Quantum Mechanical Picture of the Atom 146
 - ENRICHMENT: The Schrödinger Equation** 147
- 4-16 Quantum Numbers 147
- 4-17 Atomic Orbitals 148
- 4-18 Electron Configurations 153
- 4-19 The Periodic Table and Electron Configurations 159
- 4-20 Paramagnetism and Diamagnetism 161
 - Key Terms** 162
 - Exercises** 164

5 Chemical Periodicity 173

- 5-1 More About the Periodic Table 174

CHEMISTRY IN USE: The Periodic Table 175

PERIODIC PROPERTIES OF THE ELEMENTS 177

- 5-2 Atomic Radii 177
- 5-3 Ionization Energy 179
- 5-4 Electron Affinity 182
- 5-5 Ionic Radii 184
- 5-6 Electronegativity 186
- 5-7 Oxidation States 187

CHEMICAL REACTIONS AND PERIODICITY 190

- 5-8 Hydrogen and the Hydrides 190
- 5-9 Oxygen and the Oxides 193
 - Key Terms** 201
 - Exercises** 202

6 Some Types of Chemical Reactions 207

- 6-1 Aqueous Solutions: An Introduction 208
- 6-2 Reactions in Aqueous Solutions 215

NAMING SOME INORGANIC COMPOUNDS 217

- 6-3 Naming Binary Compounds 217
- 6-4 Naming Ternary Acids and Their Salts 219

CLASSIFYING CHEMICAL REACTIONS 222

- 6-5 Oxidation–Reduction Reactions: Introduction 222
- 6-6 Combination Reactions 225
- 6-7 Decomposition Reactions 226
- 6-8 Displacement Reactions 227

CHEMISTRY IN USE: Troublesome Displacement Reactions 230

- 6-9 Metathesis Reactions 232
- 6-10 Gas-Formation Reactions 237
- 6-11 Summary of Reaction Types 238

Key Terms 240
Exercises 241

7 Chemical Bonding 249

- 7-1 Lewis Dot Formulas of Atoms 250

IONIC BONDING 251

- 7-2 Formation of Ionic Compounds 251
 - ENRICHMENT: Introduction to Energy Relationships in Ionic Bonding** 256

COVALENT BONDING 258

- 7-3 Formation of Covalent Bonds 258
- 7-4 Bond Lengths and Bond Energies 259
- 7-5 Lewis Formulas for Molecules and Polyatomic Ions 260
- 7-6 Writing Lewis Formulas: The Octet Rule 261
- 7-7 Formal Charges 267
- 7-8 Writing Lewis Formulas: Limitations of the Octet Rule 269
- 7-9 Resonance 274

- 7-10 Polar and Nonpolar Covalent Bonds 276
- 7-11 Dipole Moments 278
- 7-12 The Continuous Range of Bonding Types 279
 - Key Terms 280
 - Exercises 281

8 Molecular Structure and Covalent Bonding Theories 287

- 8-1 A Preview of the Chapter 288
- 8-2 Valence Shell Electron Pair Repulsion Theory 290
- 8-3 Polar Molecules: The Influence of Molecular Geometry 292
- 8-4 Valence Bond Theory 293
- MOLECULAR SHAPES AND BONDING 294**
 - 8-5 Linear Electronic Geometry: AB_2 Species (No Lone Pairs on A) 295
 - 8-6 Trigonal Planar Electronic Geometry: AB_3 Species (No Lone Pairs on A) 297
 - 8-7 Tetrahedral Electronic Geometry: AB_4 Species (No Lone Pairs on A) 299
 - 8-8 Tetrahedral Electronic Geometry: AB_3U Species (One Lone Pair on A) 304
 - 8-9 Tetrahedral Electronic Geometry: AB_2U_2 Species (Two Lone Pairs on A) 308
 - 8-10 Tetrahedral Electronic Geometry: ABU_3 Species (Three Lone Pairs on A) 310
 - 8-11 Trigonal Bipyramidal Electronic Geometry: AB_5 , AB_4U , AB_3U_2 , and AB_2U_3 310
 - 8-12 Octahedral Electronic Geometry: AB_6 , AB_5U , AB_4U_2 314
 - 8-13 Lone Pairs on the Central Atom—A Summary 315
 - 8-14 Compounds Containing Double Bonds 317
 - 8-15 Compounds Containing Triple Bonds 319
 - 8-16 A Summary of Electronic and Molecular Geometries 320
 - Key Terms 322
 - Exercises 323

9 Molecular Orbitals in Chemical Bonding 329

- 9-1 Molecular Orbitals 330
- 9-2 Molecular Orbital Energy Level Diagrams 333

- 9-3 Bond Order and Bond Stability 335
- 9-4 Homonuclear Diatomic Molecules 335
- 9-5 Heteronuclear Diatomic Molecules 339
- 9-6 Delocalization and the Shapes of Molecular Orbitals 341
 - Key Terms 343
 - Exercises 344

10 Reactions in Aqueous Solutions I: Acids, Bases, and Salts 347

- 10-1 Properties of Aqueous Solutions of Acids and Bases 349
- 10-2 The Arrhenius Theory 349
- 10-3 The Hydronium Ion (Hydrated Hydrogen Ion) 350
- 10-4 The Brønsted–Lowry Theory 350
- 10-5 The Autoionization of Water 353
- 10-6 Amphoterism 354
- 10-7 Strengths of Acids 355
- 10-8 Acid–Base Reactions in Aqueous Solutions 358
 - CHEMISTRY IN USE: Everyday Salts of Ternary Acids 360**
- 10-9 Acidic Salts and Basic Salts 361
- 10-10 The Lewis Theory 363
- 10-11 The Preparation of Acids 365
 - Key Terms 367
 - Exercises 367

11 Reactions in Aqueous Solutions II: Calculations 375

- AQUEOUS ACID–BASE REACTIONS 376**
 - 11-1 Calculations Involving Molarity 376
 - 11-2 Titrations 380
 - 11-3 Calculations for Acid–Base Titrations 382
- OXIDATION–REDUCTION REACTIONS 386**
 - 11-4 Balancing Redox Equations 387
 - 11-5 Adding H^+ , OH^- , or H_2O to Balance Oxygen or Hydrogen 388
 - 11-6 Calculations for Redox Titrations 390
 - Key Terms 393
 - Exercises 393

12 Gases and the Kinetic–Molecular Theory 401

- 12-1 Comparison of Solids, Liquids, and Gases 402
- 12-2 Composition of the Atmosphere and Some Common Properties of Gases 403
- 12-3 Pressure 403
- 12-4 Boyle's Law: The Volume–Pressure Relationship 405
 - CHEMISTRY IN USE: The Greenhouse Effect and Climate Change 406
- 12-5 Charles's Law: The Volume–Temperature Relationship; The Absolute Temperature Scale 410
- 12-6 Standard Temperature and Pressure 412
- 12-7 The Combined Gas Law Equation 412
- 12-8 Avogadro's Law and the Standard Molar Volume 414
- 12-9 Summary of Gas Laws: The Ideal Gas Equation 415
- 12-10 Determination of Molecular Weights and Molecular Formulas of Gaseous Substances 419
- 12-11 Dalton's Law of Partial Pressures 420
- 12-12 Mass–Volume Relationships in Reactions Involving Gases 426
- 12-13 The Kinetic–Molecular Theory 428
 - ENRICHMENT: Kinetic–Molecular Theory, the Ideal Gas Equation, and Molecular Speeds 431
- 12-14 Diffusion and Effusion of Gases 433
- 12-15 Deviations from Ideal Gas Behavior 435
 - Key Terms 438
 - Exercises 439

13 Liquids and Solids 449

- 13-1 Kinetic–Molecular Description of Liquids and Solids 450
 - 13-2 Intermolecular Attractions and Phase Changes 451
- ### THE LIQUID STATE 458
- 13-3 Viscosity 459
 - 13-4 Surface Tension 460
 - 13-5 Capillary Action 460
 - 13-6 Evaporation 461
 - 13-7 Vapor Pressure 462
 - 13-8 Boiling Points and Distillation 464
 - 13-9 Heat Transfer Involving Liquids 465
 - ENRICHMENT: The Clausius–Clapeyron Equation 467

THE SOLID STATE 469

- 13-10 Melting Point 469
- 13-11 Heat Transfer Involving Solids 469
- 13-12 Sublimation and the Vapor Pressure of Solids 472
- 13-13 Phase Diagrams (P versus T) 472
- 13-14 Amorphous Solids and Crystalline Solids 475
 - ENRICHMENT: X-Ray Diffraction 476
- 13-15 Structures of Crystals 478
- 13-16 Bonding in Solids 481
- 13-17 Band Theory of Metals 489
 - CHEMISTRY IN USE: Semiconductors 492
 - Key Terms 494
 - Exercises 496

14 Solutions 505

THE DISSOLUTION PROCESS 506

- 14-1 Spontaneity of the Dissolution Process 506
- 14-2 Dissolution of Solids in Liquids 508
- 14-3 Dissolution of Liquids in Liquids (Miscibility) 510
- 14-4 Dissolution of Gases in Liquids 512
- 14-5 Rates of Dissolution and Saturation 513
- 14-6 Effect of Temperature on Solubility 514
- 14-7 Effect of Pressure on Solubility 515
- 14-8 Molality and Mole Fraction 516

COLLIGATIVE PROPERTIES OF SOLUTIONS 517

- 14-9 Lowering of Vapor Pressure and Raoult's Law 518
 - 14-10 Fractional Distillation 522
 - 14-11 Boiling Point Elevation 523
 - 14-12 Freezing Point Depression 525
 - 14-13 Determination of Molecular Weight by Freezing Point Depression or Boiling Point Elevation 526
 - 14-14 Colligative Properties and Dissociation of Electrolytes 527
 - 14-15 Osmotic Pressure 531
- ### COLLOIDS 535
- 14-16 The Tyndall Effect 535
 - 14-17 The Adsorption Phenomenon 535

CHEMISTRY IN USE: Water Purification and Hemodialysis 536

14-18 Hydrophilic and Hydrophobic Colloids 539**CHEMISTRY IN USE: Why Does Red Wine Go with Red Meat? 542****Key Terms 542****Exercises 543****15 Chemical Thermodynamics 551****HEAT CHANGES AND THERMOCHEMISTRY 553****15-1 The First Law of Thermodynamics 553****15-2 Some Thermodynamic Terms 555****15-3 Enthalpy Changes 556****15-4 Calorimetry: Measurement of Heat Transfer 556****15-5 Thermochemical Equations 558****15-6 Standard States and Standard Enthalpy Changes 561****15-7 Standard Molar Enthalpies of Formation, ΔH_f° 562****15-8 Hess's Law 564****15-9 Bond Energies 568****15-10 Changes in Internal Energy, ΔE 571****15-11 Relationship Between ΔH and ΔE 577****SPONTANEITY OF PHYSICAL AND CHEMICAL CHANGES 578****15-12 The Two Aspects of Spontaneity 579****15-13 Dispersal of Energy and Matter 580****15-14 Entropy, S , and Entropy Change, ΔS 583****15-15 The Second Law of Thermodynamics 589****15-16 Free Energy Change, ΔG , and Spontaneity 591****15-17 The Temperature Dependence of Spontaneity 594****Key Terms 598****Exercises 599****16 Chemical Kinetics 611****16-1 The Rate of a Reaction 613****FACTORS THAT AFFECT REACTION RATES 618****16-2 Nature of the Reactants 619****16-3 Concentrations of Reactants: The Rate-Law Expression 619****16-4 Concentration Versus Time: The Integrated Rate Equation 627****ENRICHMENT: Calculus Derivation of Integrated Rate Equations 633****ENRICHMENT: Using Integrated Rate Equations to Determine Reaction Order 634****16-5 Collision Theory of Reaction Rates 638****16-6 Transition State Theory 638****16-7 Reaction Mechanisms and the Rate-Law Expression 640****16-8 Temperature: The Arrhenius Equation 643****16-9 Catalysts 647****CHEMISTRY IN USE: Ozone 654****Key Terms 656****Exercises 657****17 Chemical Equilibrium 667****17-1 Basic Concepts 668****17-2 The Equilibrium Constant 670****17-3 Variation of K_c with the Form of the Balanced Equation 673****17-4 The Reaction Quotient 674****17-5 Uses of the Equilibrium Constant, K_c 676****17-6 Disturbing a System at Equilibrium: Predictions 679****17-7 The Haber Process: A Commercial Application of Equilibrium 686****17-8 Disturbing a System at Equilibrium: Calculations 688****17-9 Partial Pressures and the Equilibrium Constant 691****17-10 Relationship between K_p and K_c 692****17-11 Heterogeneous Equilibria 694****17-12 Relationship between ΔG_{rxn}° and the Equilibrium Constant 695****17-13 Evaluation of Equilibrium Constants at Different Temperatures 699****Key Terms 700****Exercises 700****18 Ionic Equilibria I: Acids and Bases 709****18-1 A Review of Strong Electrolytes 710****18-2 The Autoionization of Water 711****18-3 The pH and pOH Scales 713****18-4 Ionization Constants for Weak Monoprotic Acids and Bases 717****18-5 Polyprotic Acids 729****18-6 Solvolysis 732****18-7 Salts of Strong Bases and Strong Acids 733****18-8 Salts of Strong Bases and Weak Acids 733****18-9 Salts of Weak Bases and Strong Acids 736**

18-10 Salts of Weak Bases and Weak Acids 737**CHEMISTRY IN USE: Taming Dangerous Acids with Harmless Salts 738****18-11 Salts That Contain Small, Highly Charged Cations 740****Key Terms 742****Exercises 742****19 Ionic Equilibria II: Buffers and Titration Curves 749****19-1 The Common Ion Effect and Buffer Solutions 750****19-2 Buffering Action 756****19-3 Preparation of Buffer Solutions 759****CHEMISTRY IN USE: Fun with Carbonates 762****19-4 Acid–Base Indicators 763****TITRATION CURVES 765****19-5 Strong Acid/Strong Base Titration Curves 765****19-6 Weak Acid/Strong Base Titration Curves 768****19-7 Weak Acid/Weak Base Titration Curves 769****19-8 Summary of Acid–Base Calculations 771****Key Terms 772****Exercises 773****20 Ionic Equilibria III: The Solubility Product Principle 779****20-1 Solubility Product Constants 780****20-2 Determination of Solubility Product Constants 782****20-3 Uses of Solubility Product Constants 784****ENRICHMENT: The Effects of Hydrolysis on Solubility 787****20-4 Fractional Precipitation; $Q_{sp} \geq K_{sp}$ 790****20-5 Simultaneous Equilibria Involving Slightly Soluble Compounds 792****20-6 Dissolving Precipitates; $Q_{sp} < K_{sp}$ 795****Key Terms 797****Exercises 798****21 Electrochemistry 803****21-1 Electrical Conduction 805****21-2 Electrodes 805****ELECTROLYTIC CELLS 805****21-3 The Electrolysis of Molten Sodium Chloride (The Downs Cell) 806****21-4 The Electrolysis of Aqueous Sodium Chloride 807****21-5 The Electrolysis of Aqueous Sodium Sulfate 808****21-6 Counting Electrons: Coulometry and Faraday's Law of Electrolysis 808****CHEMISTRY IN USE: A Spectacular View of One Mole of Electrons 810****21-7 Commercial Applications of Electrolytic Cells 811****VOLTAIC OR GALVANIC CELLS 811****21-8 The Construction of Simple Voltaic Cells 812****21-9 The Zinc–Copper Cell 813****21-10 The Copper–Silver Cell 815****STANDARD ELECTRODE POTENTIALS 816****21-11 The Standard Hydrogen Electrode 817****21-12 The Zinc–SHE Cell 817****21-13 The Copper–SHE Cell 818****21-14 Standard Electrode Potentials 819****21-15 Uses of Standard Electrode Potentials 821****21-16 Standard Electrode Potentials for Other Half-Reactions 823****21-17 Corrosion 825****21-18 Corrosion Protection 827****EFFECT OF CONCENTRATIONS (OR PARTIAL PRESSURES) ON ELECTRODE POTENTIALS 827****21-19 The Nernst Equation 827****21-20 Using Electrochemical Cells to Determine Concentrations 832****ENRICHMENT: Concentration Cells 834****21-21 The Relationship of E_{cell}^0 to ΔG^0 and K_{eq} 835****PRIMARY VOLTAIC CELLS 836****21-22 Dry Cells 837****SECONDARY VOLTAIC CELLS 838****21-23 The Lead Storage Battery 838****21-24 The Nickel–Cadmium (Nicad) Cell 840****21-25 The Hydrogen–Oxygen Fuel Cell 840****Key Terms 842****Exercises 843**

22 Nuclear Chemistry 851

- 22-1 The Nucleus 853
- 22-2 Neutron-Proton Ratio and Nuclear Stability 853
- 22-3 Nuclear Stability and Binding Energy 854
- 22-4 Radioactive Decay 857
- 22-5 Equations for Nuclear Reactions 858
- 22-6 Neutron-Rich Nuclei (Above the Band of Stability) 859
- 22-7 Neutron-Poor Nuclei (Below the Band of Stability) 859
- 22-8 Nuclei with Atomic Number Greater Than 83 860
- 22-9 Detection of Radiation 861
- 22-10 Rates of Decay and Half-Life 863
- 22-11 Decay Series 865
- 22-12 Uses of Radionuclides 865

CHEMISTRY IN USE: Household Radon Exposure and Lung Cancer 869

- 22-13 Artificial Transmutations of Elements 871
- 22-14 Nuclear Fission 874
- 22-15 Nuclear Fission Reactors 876
- 22-16 Nuclear Fusion 879

CHEMISTRY IN USE: Managing Nuclear Wastes 880

Key Terms 882
Exercises 883

23 Organic Chemistry I: Formulas, Names, and Properties 887

SATURATED HYDROCARBONS 890

- 23-1 Alkanes and Cycloalkanes 890
- 23-2 Naming Saturated Hydrocarbons 895

UNSATURATED HYDROCARBONS 899

- 23-3 Alkenes 899

CHEMISTRY IN USE: Petroleum 900

- 23-4 Alkynes 905

AROMATIC HYDROCARBONS 906

- 23-5 Benzene 906
- 23-6 Other Aromatic Hydrocarbons 907

CHEMISTRY IN USE: Nanotechnology 908

- 23-7 Hydrocarbons: A Summary 910

FUNCTIONAL GROUPS 911

- 23-8 Organic Halides 911
- 23-9 Alcohols and Phenols 913

CHEMISTRY IN USE: Developing More Environmentally Friendly Solvents 914

- 23-10 Ethers 918
- 23-11 Aldehydes and Ketones 918
- 23-12 Amines 921
- 23-13 Carboxylic Acids 922

CHEMISTRY IN USE: The Chemistry of Artists' Pigments 924

- 23-14 Some Derivatives of Carboxylic Acids 926

CHEMISTRY IN USE: Butter, Margarine, and *trans* Fats 930

- 23-15 Summary of Functional Groups 930

FUNDAMENTAL CLASSES OF ORGANIC REACTIONS 932

- 23-16 Substitution Reactions 932
- 23-17 Addition Reactions 935
- 23-18 Elimination Reactions 937
- 23-19 Polymerization Reactions 938

Key Terms 943
Exercises 944

24 Organic Chemistry II: Shapes, Selected Reactions, and Biopolymers 953

SHAPES OF ORGANIC MOLECULES 954

- 24-1 Constitutional Isomers 954
- 24-2 Stereoisomers 955
- 24-3 Conformations 959

SELECTED REACTIONS 960

- 24-4 Reactions of Brønsted-Lowry Acids and Bases 960
- 24-5 Oxidation-Reduction Reactions 963

CHEMISTRY IN USE: Chemical Communication 964

- 24-6 Formation of Carboxylic Acid Derivatives 968
- 24-7 Hydrolysis of Esters 969

BIOPOLYMERS 970

- 24-8 Carbohydrates 971
- 24-9 Polypeptides and Proteins 974
- 24-10 Nucleic Acids 978

CHEMISTRY IN USE: The Cells' Drinking Straws 979

Key Terms 982
Exercises 983

25 Coordination Compounds 989

- 25-1 Coordination Compounds 990
- 25-2 Ammine Complexes 993
- 25-3 Important Terms 994
- 25-4 Nomenclature 995
- 25-5 Structures 998

ISOMERISM IN COORDINATION COMPOUNDS 998

- 25-6 Structural (Constitutional) Isomers 999
- 25-7 Stereoisomers 1000

BONDING IN COORDINATION COMPOUNDS 1006

- 25-8 Crystal Field Theory 1006
- 25-9 Color and the Spectrochemical Series 1008

Key Terms 1010

Exercises 1011

26 Metals I: Metallurgy 1017

METALS 1018

- 26-1 Occurrence of the Metals 1018

METALLURGY 1018

- 26-2 Pretreatment of Ores 1019
- 26-3 Reduction to the Free Metals 1021
- 26-4 Refining of Metals 1022

METALLURGIES OF SPECIFIC METALS 1023

- 26-5 Magnesium 1023
- 26-6 Aluminum 1024
- 26-7 Iron 1026
- 26-8 Copper 1028
- 26-9 Gold 1029

Key Terms 1030

Exercises 1030

27 Metals II: Properties and Reactions 1035

THE ALKALI METALS (GROUP 1A) 1036

- 27-1 Group 1A Metals: Properties and Occurrence 1036
- 27-2 Reactions of the Group 1A Metals 1037

CHEMISTRY IN USE: Trace Elements and Life 1038

- 27-3 Uses of Group 1A Metals and Their Compounds 1041

THE ALKALINE EARTH METALS (GROUP 2A) 1042

- 27-4 Group 2A Metals: Properties and Occurrence 1042
- 27-5 Reactions of the Group 2A Metals 1042
- 27-6 Uses of Group 2A Metals and Their Compounds 1043

THE POST-TRANSITION METALS 1045

- 27-7 Group 3A: Periodic Trends 1045

CHEMISTRY IN USE: The Most Valuable Metal in the World 1047

THE *d*-TRANSITION METALS 1048

- 27-8 General Properties 1049
- 27-9 Oxidation States 1049
- 27-10 Chromium Oxides, Oxyanions, and Hydroxides 1050

CHEMISTRY IN USE: Our Love–Hate Relationship with Mercury 1052

Key Terms 1053

Exercises 1053

28 Some Nonmetals and Metalloids 1057

THE NOBLE GASES (GROUP 8A) 1058

- 28-1 Occurrence, Uses, and Properties 1058
- 28-2 Xenon Compounds 1059

THE HALOGENS (GROUP 7A) 1059

- 28-3 Properties 1060
- 28-4 Occurrence, Production, and Uses 1061
- 28-5 Reactions of the Free Halogens 1062
- 28-6 The Hydrogen Halides and Hydrohalic Acids 1063
- 28-7 The Oxoacids (Ternary Acids) of the Halogens 1064

SULFUR, SELENIUM, AND TELLURIUM 1065

- 28-8 Occurrence, Properties, and Uses 1065
- 28-9 Reactions of Group 6A Elements 1067
- 28-10 Hydrides of Group 6A Elements 1067
- 28-11 Group 6A Oxides 1068
- 28-12 Oxoacids of Sulfur 1069

NITROGEN AND PHOSPHORUS 1070

- 28-13 Occurrence of Nitrogen 1071
- 28-14 Hydrogen Compounds of Nitrogen 1072
- 28-15 Nitrogen Oxides 1073

CHEMISTRY IN USE: Nitrogen Oxides and Photochemical Smog 1075

28-16 Some Oxoacids of Nitrogen and Their Salts 1076

28-17 Phosphorus 1077

SILICON 1078

28-18 Silicon and the Silicates 1078

Key Terms 1080

Exercises 1080

APPENDIX A Some Mathematical Operations A-1

APPENDIX B Electronic Configurations of the Atoms of the Elements A-9

APPENDIX C Common Units, Equivalences, and Conversion Factors A-12

APPENDIX D Physical Constants A-15

APPENDIX E Some Physical Constants for a Few Common Substances A-16

APPENDIX F Ionization Constants for Weak Acids at 25°C A-18

APPENDIX G Ionization Constants for Weak Bases at 25°C A-20

APPENDIX H Solubility Product Constants for Some Inorganic Compounds at 25°C A-21

APPENDIX I Dissociation Constants for Some Complex Ions A-23

APPENDIX J Standard Reduction Potentials in Aqueous Solution at 25°C A-24

APPENDIX K Selected Thermodynamic Values at 298.15 K A-27

APPENDIX L Answers to Selected Even-Numbered Numerical Exercises A-30

Index of Equations E-1

Glossary/Index I-1

About the Authors

KEN WHITTEN is Professor Emeritus at the University of Georgia. Dr. Whitten received his A.B. at Berry College, M.S. at the University of Mississippi, and Ph.D. at the University of Illinois. He taught at Tulane, the University of Southwestern Louisiana, the Mississippi State College for Women, and the University of Alabama, before joining the UGA faculty as Assistant Professor and Coordinator of General Chemistry in 1967. He remained Coordinator of General Chemistry throughout his UGA career until his retirement in 1998. His numerous awards include the G. E. Philbrook Chemistry Teacher of the Year Award, the Outstanding Honor's Professor, the Franklin College Outstanding Teacher of the Year, the General Sandy Beaver Teaching Award, and a Senior Teaching Fellowship. An award was established in Dr. Whitten's honor in 1998 celebrating outstanding teaching assistants in UGA's department of chemistry.



RAY DAVIS is University Distinguished Teaching Professor Emeritus at the University of Texas at Austin. He received his B.S. at the University of Kansas in 1960 and his Ph.D. from Yale University in 1965. He was a Cancer Research Scientist at the Roswell Park Memorial Institute from 1964 to 1966. His many teaching awards include the Minnie Stevens Piper Professorship in

1992, the Jean Holloway Award for Excellence in Teaching in 1996, and (five times) the Outstanding Teacher Award given by campus freshman honor societies. In 1995 he was named an inaugural member of the University's Academy of Distinguished Teachers. His friends and former students have created the Raymond E. Davis Endowed Scholarship in Chemistry and Biochemistry in his honor.



M. LARRY PECK is Professor Emeritus at Texas A&M University. He received his Ph.D. from Montana State University in 1971. He won the Catalyst Award (a national award for excellence in chemistry teaching) presented by the Chemical Manufacturers Association in 2000, Texas A&M's Association of Former Students Distinguished Achievement Award in Chemistry

Teaching in 2002, and the Division of Chemical Education's Outstanding Service to the Division Award in 2007. Until his retirement in 2006, Dr. Peck was very active in teaching science at all levels and directed workshops designed to improve the teaching of physical science programs now known in Texas as "integrated physics and chemistry." The resource materials developed in these workshops are currently being used as models for other state-funded teacher training programs. His colleagues, friends, and former students created the M. Larry Peck Endowed Scholarship in Chemistry.



GEORGE STANLEY, Cyril & Tutta Vetter Alumni Professor at Louisiana State University, received his B.S. from the University of Rochester in 1975 and his Ph.D. from Texas A&M University in 1979. He has extensive research experience in inorganic and catalytic chemistry. George has received numerous awards and accolades, both nationally and locally, including the

NSF Special Creativity Awards in 1994 and 2003, the LSU University Excellence in Teaching Award in 1995, the LSU College of Basic Sciences Teaching Award, the Baton Rouge-ACS Charles F. Coates Award in 1999, and American Chemical Society Fellow in 2011. George was Chair of the 2005 Inorganic Chemistry Gordon Research Conference and organizer of the NSF Inorganic Chemistry Workshops from 1996 through 1999. He was named 2005–2006 TIAA-CREF Service Learning Fellow for his longtime commitment to service-learning programs at LSU.

For the Instructor

Chemistry and *Chemistry with Qualitative Analysis Supplement*, tenth edition, are intended for use in the introductory chemistry course taken by students of chemistry, biology, geology, physics, engineering, and related subjects. Although some background in high school science is helpful, no specific knowledge of topics in chemistry is presupposed. This book has self-contained presentations of the fundamentals of chemistry. The aim is to convey to students the dynamic and changing aspects of chemistry in the modern world.

This text provides a means by which students can develop an understanding of fundamental concepts of chemistry; the students' ability to solve problems is based on this understanding. Our goal in this revision is to provide students with the best possible tool for learning chemistry by incorporating and amplifying features that enhance their understanding of concepts and guide them through the more challenging aspects of learning chemistry.

What's New

Chemistry, 10th edition, Summary of Changes

This new edition of *Chemistry* continues to incorporate a strong molecular reasoning focus, amplified problem-solving exercises, a wide range of real-life examples and applications, and innovative technological resources. With this text's focus on molecular reasoning, your students will learn to think at the molecular level and make connections between molecular structure and macroscopic properties. The tenth edition has been revised throughout and now includes a reorganization of the descriptive chemistry chapters to improve the flow of topics, a new basic math skills appendix, an updated art program with new "talking labels" that fully explain what is going on in the figure, and much more.

9th edition	10th edition	Notes
1. The Foundations of Chemistry	1. The Foundations of Chemistry	- NEW BASIC MATH SKILLS APPENDIX: To aid the flow of introductory chemistry material in Chapter 1, a review of topics in basic mathematics skills, including scientific notation and use of significant figures, with numerous examples, now appears in Appendix A. Related exercises remain in the "Measurements and Calculations" section at the end of Chapter 1. - New chapter-opening photo presentation introducing students to the concept that chemistry is everywhere! - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - Updated "Chemistry in Use: Names of the Elements." 20% new and revised end-of-chapter exercises. - Expanded "Beyond the Textbook" section now includes "Chemistry in Use" essay questions.
2. Chemical Formulas and Composition Stoichiometry	2. Chemical Formulas and Composition Stoichiometry	- Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - This chapter introduces the use of effective visual representations of molecules—chemical and structural formulas, ball-and-stick and space-filling models—throughout the text to facilitate student appreciation of shapes and properties of molecules. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - This early coverage of basic concepts such as the mole, atomic weights, ions and ionic charges, molecules, and formulas and composition provides an effective groundwork for subsequent study and calculations in chemistry. 20% new and revised end-of-chapter exercises. - Expanded "Beyond the Textbook" section now includes "Chemistry in Use" essay questions.

9th edition	10th edition	Notes
3. Chemical Equations and Reaction Stoichiometry	3. Chemical Equations and Reaction Stoichiometry	- New chapter-opening photo presentation on the combustion of methane with oxygen featuring integrated displays of various chemical representations, including models (space-filling, ball-and-stick), chemical formulas (molecules and equations), and reacting systems. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New stoichiometry formula balancing example added to cover the concept of fractional coefficients and the various ways of dealing with them. - New reaction ratio labels added to examples to clarify this concept to students. - Two new “Stop & Think” boxes added to help students with reaction balancing. Several other existing “Stop & Think” boxes edited to improve their helpfulness and clarity. - The basic concepts introduced in the previous chapter provide the basis for understanding reaction stoichiometry and develop student familiarity with writing, balancing, interpreting, and calculating with chemical equations. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - Calculation skills learned in previous chapters help students build facility and confidence in working with chemical reactions, equations, and solutions. 20% new and revised end-of-chapter exercises.
4. The Structure of Atoms	4. The Structure of Atoms	- New chapter-opening photo presentation emphasizing the connection of colors and energy of light to understanding atomic structure. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. Revised and updated artwork for over 40% of the figures in this chapter. - Systematic presentation of the historic development of atomic theory helps students understand chemical thought and appreciate central ideas of the science. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - The systematic introduction of light, energy, and subatomic particles aids in student appreciation of the central ideas of atomic theory and the periodic table of the elements. - Updated “Chemistry in Use: Stable Isotope Ratio Analysis.” 20% new and revised end-of-chapter exercises. - Expanded “Beyond the Textbook” section now includes “Chemistry in Use” essay questions.
5. Chemical Periodicity	5. Chemical Periodicity	- Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - Coordinated presentation of basic aspects of atomic structure with observed properties of elements and compounds enhance student appreciation of the periodic table in correlating the versatile use and power of the periodic table. - Updated “Chemistry in Use: The Periodic Table” and “The Discovery of Phosphorus” combined and edited. - New text addition to explain the size discrepancies between Te and Po relative to lighter elements in their column. - Improved discussion of hydrides and related binary compounds with hydrogen. - Reorganized discussion of metal oxides to improve clarity and flow. 20% new and revised end-of-chapter exercises. - Expanded “Beyond the Textbook” section now includes “Chemistry in Use” essay questions.
6. Some Types of Chemical Reactions	6. Some Types of Chemical Reactions	- REORGANIZED INTRODUCTION TO AQUEOUS SOLUTIONS: Section 6-1 has been completely reorganized to improve the descriptive introduction to aspects of aqueous solutions, including ionization and dissociation, acids, bases, and solubility guidelines. These basic ideas are then elaborated in the classification of reactions in the remainder of Chapter 6 and serve as a foundation throughout the textbook for further discussion of physical and chemical properties of solutions. - New chapter-opening photo presentation on precipitation reaction of AgNO_3 and potassium iodide. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - Revised acid–base labeling color scheme that parallels the color scheme for the electrostatic charge potential surfaces on molecules for improved consistency throughout text (red for buildup of negative charge for bases; blue for cationic charge on H^+). - Revised oxidation number labeling system for easier student correlation with chemical formulas. - Updated tabular presentation of acids, bases, and other industrial chemicals. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - Updated “Chemistry in Use: Troublesome Displacement Reactions.” 20% new and revised end-of-chapter exercises. - Expanded “Beyond the Textbook” section now includes “Chemistry in Use” essay questions.
7. Chemical Bonding	7. Chemical Bonding	- Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - Many edits to clarify discussions of bonding concepts, especially for working out Lewis dot structures. - Consistent verbal and visual distinction between ionic bonding (electron <i>transfer</i>) and covalent bonding (electron <i>sharing</i>) to aid student understanding. - Updated and new “Problem-Solving Tips” enhance student use of versatile, effective strategies for writing and understanding Lewis formulas and electron distributions in covalent molecules and ions. 20% new and revised end-of-chapter exercises. - Expanded “Beyond the Textbook” section now includes “Chemistry in Use” essay questions.

9th edition	10th edition	Notes
8. Molecular Structure and Covalent Bonding Theories	8. Molecular Structure and Covalent Bonding Theories	- An expanded section including a more comprehensive, tabular summary of the influence of central atom lone pairs on molecular geometry has been added in Chapter 8, enhancing student understanding of this key concept. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. 20% new and revised end-of-chapter exercises.
9. Molecular Orbitals in Chemical Bonding	9. Molecular Orbitals in Chemical Bonding	- Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless.
10. Reactions in Aqueous Solutions I: Acids, Bases, and Salts	10. Reactions in Aqueous Solutions I: Acids, Bases, and Salts	- New chapter-opening photo presentation on the chemistry of an Alka-Seltzer tablet in water. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. 20% new and revised end-of-chapter exercises. - Expanded “Beyond the Textbook” section now includes “Chemistry in Use” essay questions.
11. Reactions in Aqueous Solutions II: Calculations	11. Reactions in Aqueous Solutions II: Calculations	- New chapter-opening photo presentation illustrating the use of purple potassium permanganate as an internal indicator. - New margin notes and “Stop & Think” boxes clarify more difficult concepts to students. - New oxidation state symbols and text edits further clarify redox equation balancing to students. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. 20% new and revised end-of-chapter exercises.
12. Gases and the Kinetic-Molecular Theory	12. Gases and the Kinetic-Molecular Theory	- New chapter-opening photo showing the lower density of gases with increasing temperature via hot air balloons. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - Updated “Chemistry in Use: The Greenhouse Effect and Climate Change” to help students understand current scientific knowledge regarding this important environmental issue. “Problem-Solving Tips” and “Stop & Think” features are further enhanced to help students develop and analyze the use of proper units in gas law calculations. - New inclusion of the Maxwell-Boltzmann distribution function helps student appreciation and use of this important concept in gas molecular behavior. 20% new and revised end-of-chapter exercises. - Expanded “Beyond the Textbook” section now includes “Chemistry in Use” essay questions.
13. Liquids and Solids	13. Liquids and Solids	- New chapter-opening photo presentation on interfacial force microscopy and how water wets a metal surface. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New electrostatic charge potential surfaces help students visualize and better understand the differences between nonpolar and polar molecules. - Consistent discussion of intermolecular forces and attractions in substances, coupled with the dramatic visual presentation, builds student understanding of physical properties and transitions of condensed phases of matter. - Fully revised Figure 13-13 on vapor pressure, boiling points, and polarity including ECP molecular images. Substantial edits on figure captions and text for this section. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - Updated “Chemistry in Use: Semiconductors.” 20% new and revised end-of-chapter exercises. - Expanded “Beyond the Textbook” section now includes “Chemistry in Use” essay questions.
14. Solutions	14. Solutions	- New chapter-opening photo presentation on spreading soluble salt for control of ice and snow on roadways. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - Several examples were updated with corrected calculations, making them clearer for students. - Concepts and skills developed in prior chapters are consistently applied to enhance student grasp of solutions and their properties. - Basic concepts of intermolecular energies and attractions from prior chapters help students develop knowledge and calculations regarding colligative properties. - New ECP molecular images continue to reinforce the key concepts of polarity and intermolecular attractive forces. - The importance of colloids in biology and daily life is emphasized along with a new photograph more clearly showing the Tyndall effect. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - Updated “Chemistry in Use: Water Purification and Hemodialysis” and “Why Does Red Wine Go with Red Meat?” 20% new and revised end-of-chapter exercises. - Expanded “Beyond the Textbook” section now includes “Chemistry in Use” essay questions.

9th edition	10th edition	Notes
15. Chemical Thermodynamics	15. Chemical Thermodynamics	- New chapter-opening photo presentation on windmills as an environmentally “green” source of electricity. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. The critical central nature of the concepts of energy in chemistry and chemical change is thoroughly explored. - The key concept of entropy as an assessment of dispersal of matter and of energy is carefully developed to provide a firm foundation for later ideas, including heat changes that accompany chemical and physical changes, prediction of reactions, and chemical bond stability. Throughout this chapter, many fundamental terms are rigorously defined, discussed, and illustrated for use throughout later studies of chemistry. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. 20% new and revised end-of-chapter exercises.
16. Chemical Kinetics	16. Chemical Kinetics	- New, more dramatic chapter-opening photo presentation on an exothermic reaction using an example of a burning building. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - Chemical principles introduced in prior chapters are used to define rates of chemical reactions and describe basic approaches to calculating and controlling reaction rates. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - Careful distinctions between the rate-law and the integrated rate-law expressions are used to build student understanding of the analysis and control of chemical reaction rates. - Bonding and molecular considerations presented in prior chapters allow student understanding of reaction mechanisms and their influence on the rate-law expression. - Interpretation of the Maxwell-Boltzmann energy distribution, introduced in Chapter 12, further aids student appreciation of the significance of temperature and catalysts in the control of chemical reaction rates. - Updated “Chemistry in Use: Ozone.” 20% new and revised end-of-chapter exercises. - Expanded “Beyond the Textbook” section now includes “Chemistry in Use” essay questions.
17. Chemical Equilibrium	17. Chemical Equilibrium	- New chapter-opening photo presentation on chemical equilibrium. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - Example 17-5 expanded to better explain the concepts and answers. - Concepts presented in this and the two preceding chapters give students an integrated insight into some central issues in chemistry: Why and in which direction does the reaction proceed? How fast does it proceed? and How far does it proceed? The critical use of the equilibrium constant summarizes these critical interpretations. - Important concepts in prior chapters are utilized to aid student use of LeChatelier’s Principle—predicting and calculating the effects on reaction direction and extent when temperature, pressures, concentrations, and other reaction conditions are altered. - A number of small edits and new margin notes to clarify the key concepts introduced in this chapter. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. 20% new and revised end-of-chapter exercises.
18. Ionic Equilibria I: Acids and Bases	18. Ionic Equilibria I: Acids and Bases	- Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - The principles of chemical equilibrium already presented are utilized in the next three chapters to organize student treatment of equilibrium in aqueous solutions that contain weak or strong ionic solutes and their mixtures—acids, bases, and salts. - Updated “Chemistry in Use: Taming Dangerous Acids with Harmless Salts.” 20% new and revised end-of-chapter exercises. - Expanded “Beyond the Textbook” section now includes “Chemistry in Use” essay questions.
19. Ionic Equilibria II: Buffers and Titration Curves	19. Ionic Equilibria II: Buffers and Titration Curves	- Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. - Updated “Chemistry in Use: Fun with Carbonates.” 20% new and revised end-of-chapter exercises. - Expanded “Beyond the Textbook” section now includes “Chemistry in Use” essay questions.
20. Ionic Equilibria III: The Solubility Product Principle	20. Ionic Equilibria III: The Solubility Product Principle	- New chapter-opening presentation on mineral formation in caves. - Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. - New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. 20% new and revised end-of-chapter exercises.

9th edition	10th edition	Notes
21. Electrochemistry	21. Electrochemistry	• New chapter-opening presentation on electrochemistry featuring Nellis Air Force Base's solar panel system. • Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. Over 30% of the artwork was revised to more clearly illustrate the concepts being taught. • Central ideas from prior chapters help students gain understanding of the functions of important electrochemical cells: (a) electrolytic cells in which external electrical energy causes otherwise nonspontaneous chemical reactions to occur and (b) voltaic cells in which spontaneous reactions produce electricity. • Earlier techniques are used to help students learn to balance chemical reactions in electrochemical cells. • Knowledge of oxidation and reduction processes from earlier chapters helps students gain a better ability to recognize these processes in electrochemical cells. • Students learn to use standard electrode potentials to predict cell voltage and spontaneity in voltaic cells. • Skills from earlier chapters are used to assess the effects of changing concentrations in electrochemical cells. • The fundamental ideas of free energy electrode potentials and chemical equilibrium are carefully compared to illustrate the interrelationships of these key chemical concepts. • Earlier concepts shed light on useful practical cells such as batteries, dry cells, and fuel cells. • New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. • 20% new and revised end-of-chapter exercises. • Expanded "Beyond the Textbook" section now includes "Chemistry in Use" essay questions.
22. Metals I: Metallurgy	22. Nuclear Chemistry	• Earlier presentation of nuclear chemistry is based on feedback from instructors on the order of topics most commonly taught in their programs. • Redesigned art and updated photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. • New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. • New "Chemistry in Use: Household Radon Exposure and Lung Cancer." Updated "Chemistry in Use: Managing Nuclear Wastes." • Expanded "Beyond the Textbook" section now includes "Chemistry in Use" essay questions.
23. Metals II: Properties and Reactions	23. Organic Chemistry I: Formulas, Names, and Properties	• Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. • New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. • Section 23-1 rewritten and reorganized to more clearly describe the different kinds of isomers. • Updated art on polyaromatic systems showing localized double bond structures and not coincident aromatic rings. • Updated "Chemistry in Use" boxes: "Petroleum," "Nanotechnology," "Developing More Environmentally Friendly Solvents," "The Chemistry of Artists' Pigments," and "Butter, Margarine, and trans Fats." • Expanded "Beyond the Textbook" section now includes "Chemistry in Use" essay questions.
24. Some Nonmetals and Metalloids	24. Organic Chemistry II: Shapes, Selected Reactions, and Biopolymers	• Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. • New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. • New expanded section on optical isomers that includes figures on the polarization of light and polarimetry. • Expanded "Beyond the Textbook" section now includes "Chemistry in Use" essay questions.
25. Coordination Compounds	25. Coordination Compounds	• Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. • New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. • Expanded "Beyond the Textbook" section now includes "Chemistry in Use" essay questions.
26. Nuclear Chemistry	26. Metals I: Metallurgy	• New chapter-opening photo presentation on the 21 minerals present in ore; presentation includes detailed diagram of mineral names shown in the photo. • Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. • New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. • Expanded "Beyond the Textbook" section now includes "Chemistry in Use" essay questions.
27. Organic Chemistry I: Formulas, Names, and Properties	27. Metals II: Properties and Reactions	• Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. • New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. • Updated "Chemistry in Use" boxes: "Trace Elements and Life" and "The Most Valuable Metal in the World;" new "Chemistry in Use: Our Love-Hate Relationship with Mercury." • Expanded "Beyond the Textbook" section now includes "Chemistry in Use" essay questions.
28. Organic Chemistry II: Shapes, Selected Reactions, and Biopolymers	28. Some Nonmetals and Metalloids	• Redesigned art and photography program captures the excitement of chemistry and includes integrated talking label system that aids student understanding of key concepts. • New customized table designs organize important data in an accessible, easy-to-read format, making the task of gathering and analyzing data seamless. • Updated "Chemistry in Use: Nitrogen Oxides and Photochemical Smog." • Expanded "Beyond the Textbook" section now includes "Chemistry in Use" essay questions.

Significant Features of the Tenth Edition

Atomic Structure, Periodicity, and Chemical Reactions

Increased emphasis on atomic structure as the foundation of chemistry is achieved by moving the atomic structure chapter to an earlier position, Chapter 4. That chapter includes an early, brief introduction to the periodic table. The key concept of chemical periodicity is then elaborated in more detail in Chapter 5. Instructors that wish to use an “atoms first” approach can easily start with Chapters 4 and 5, then return to stoichiometry concepts in Chapters 2 and 3. Because much of chemistry involves chemical reactions, we have introduced chemical reactions in a simplified, systematic way early in the text (Chapter 6). This placement allows us to build solidly on the ideas of atomic structure and chemical periodicity from the preceding two chapters.

Reorganized Chapters

The descriptive chemistry chapters have been moved to the back of the book as many programs do not teach this material. We still consider it important, certainly as reference material for students that keep the textbook. Nuclear chemistry and the two organic chapters were moved up to immediately follow Chapter 21 on electrochemistry. Based on our discussions with faculty at many programs, these are more typically taught after electrochemistry.

Improved Art

The richly detailed art program has been further enhanced for the tenth edition. It includes new molecular models generated by the latest software to enhance the molecular reasoning theme. Many models (both ball-and-stick and space-filling models) have been drawn to more accurately represent the molecular world and to increase students' conceptual understanding. New electrostatic charge potential (ECP) plots are included. These ECP plots, which illustrate charge distributions within molecules, help students visualize the effects of the charge distributions on molecular properties and on intermolecular interactions. To emphasize the conceptual understanding, most ECP plots show a superimposed ball-and-stick model. The ECP art often includes a color scale to aid in its interpretation.

Other Proven Features

- ▶ As in previous editions, we have reviewed the entire text and have edited the narrative for increased clarity.
- ▶ “Beyond the Textbook” exercises at the ends of chapters direct students to sources outside the textbook, such as websites, for information to use in solving these problems.
- ▶ We have included a very useful *Index of Equations*, which lists important and commonly used equations in this course.
- ▶ “**Conceptual Exercises**” in the end-of-chapter problem sets emphasize conceptual understanding rather than computation.
- ▶ The margin notes called “**Stop & Think**” alert students to common mistakes and emphasize how to recognize and avoid them. These notes, associated with both the narrative and the examples, gently remind students of possible misconceptions about a topic or procedure and emphasize points often overlooked by students.
- ▶ The “**Stop & Think**” features are also used to help students develop the skill of making qualitative checks of the reasonableness of solutions to examples.
- ▶ A **chapter outline** and a list of **objectives** are provided at the beginning of each chapter. These allow students to preview the chapter prior to reading it and help them to

Unless otherwise noted, all content on this page is © Cengage Learning.

know the expectations of the chapter. Objectives pertinent to the molecular reasoning theme have been denoted by the small molecular reasoning icon.

- ▶ **Margin notes** are used to point out historical facts, provide additional information, further emphasize some important points, relate information to ideas developed earlier, and note the relevance of discussions.
- ▶ **Key terms** are emphasized in boldface or italic type in the text and are defined at the end of each chapter, immediately reinforcing terminology and concepts.
- ▶ Many **figures** have been redrawn to improve appearance and clarity, and new photographs have been added to illustrate important points and provide visual interest.
- ▶ **“Problem-Solving Tips”** are found in almost every chapter. These highlighted helpful hints guide students through more complex subject areas. Based on the authors’ experiences and sensitivity to difficulties that the students encounter, these tips work in tandem with the “Stop & Think” feature.
- ▶ **“Chemistry in Use”** boxes, a successful feature from previous editions, have been retained and updated as needed.
- ▶ **“Enrichment”** sections provide more insight into selected topics for better-prepared students, but they can be easily omitted without any loss of continuity.
- ▶ **Titles appear on each example** so that students can see more clearly what concept or skill the example is explaining. This is also useful for review purposes before exams. Each example also contains a plan that explains the logic used to solve the problem. A note at the end of most examples, “You should now work Exercise X,” encourages students to practice appropriate end-of-chapter exercises and more closely ties illustrative examples to related exercises, thereby reinforcing concepts.
- ▶ The **exercises** at the end of each chapter have been carefully examined and revised. Approximately one-fourth of the problems are new or modified. All exercises have been carefully reviewed for accuracy. The “Building Your Knowledge” category in the end-of-chapter exercises asks students to apply knowledge they learned in previous chapters to the current chapter. These questions help students retain previously learned information and show them that chemistry is an integrated science.
- ▶ A **glossary** is included in the index so that students can look up a term at the back of the book, as well as in the “Key Terms” at the end of the chapter.

We have also continued to implement many ideas and teaching philosophies developed over the previous nine editions of this text:

We have kept in mind that chemistry is an experimental science and have emphasized the important role of theory in science. We have presented many of the classic experiments, followed by interpretations and explanations of these milestones in the development of scientific thought.

We have defined each new term as accurately as possible and illustrated its meaning as early as was practical. We begin each chapter at a fundamental level and then progress through carefully graded steps to a reasonable level of sophistication. Numerous illustrative examples are provided throughout the text and keyed to end-of-chapter exercises. The first examples in each section are quite simple; the last is considerably more complex. The unit-factor method has been emphasized where appropriate.

We believe that the central concepts of chemical change are best understood in the sequence of chemical thermodynamics (*Is the forward or the reverse reaction favored?*), followed by chemical kinetics (*How fast does the reaction go?*), and then by chemical equilibrium (*How far does the reaction go?*). Our presentation in Chapters 15 through 17 reflects this belief.

We have used color extensively to make it easier to read the text and comprehend its organization. A detailed description of our pedagogical use of color starts on page xxviii in the “For the Student” section. Pedagogical use of color makes the text clearer, more accurate, and easier to understand.

We have used a blend of SI and more traditional metric units, because many students plan careers in areas in which SI units are not yet widely used. The health care fields, the biological sciences, textiles, and agriculture are typical examples. We have used the joule rather than the calorie in nearly all energy calculations. We have emphasized the use of natural logarithms in mathematical relationships and problems, except where common practice retains the use of base-10 logarithms, such as in pH and related calculations and in the Nernst equation.

Organization

There are 28 chapters in *Chemistry*, and eight additional chapters in *A Qualitative Analysis Supplement*.

To emphasize and reinforce the molecular reasoning aspect of the text, we introduce atoms and molecules in Chapter 1. Here we discuss Dalton's atomic theory, the atom's fundamental particles, and basic models of molecules.

We present stoichiometry (Chapters 2 and 3) before atomic structure and bonding (Chapters 4–9) to establish a sound foundation for a laboratory program as early as possible. The stoichiometry chapters are virtually self-contained to provide flexibility to those who want to cover structure and bonding before stoichiometry. But instructors that want to use an “atoms first” approach can easily start with Chapters 4 and 5, then return to stoichiometry concepts in Chapters 2 and 3.

Because much of chemistry involves chemical reactions, we have introduced chemical reactions in a simplified, systematic way early in the text (Chapter 6). This placement allows us to build solidly on the ideas of atomic structure and chemical periodicity from the preceding two chapters. Our simplified, but systematic, presentation of chemical reactions in Chapter 6 builds on the ideas of atomic structure (Chapter 4) and chemical periodicity (Chapter 5). A logical, orderly introduction to formula unit, total ionic, and net ionic equations is included so that this information can be used throughout the remainder of the text. Solubility guidelines are clarified in this chapter so that students can use them in writing chemical equations in their laboratory work. Finally, naming inorganic compounds gives students early exposure to systematic nomenclature.

Many students have difficulty systematizing and using information, so we have done our utmost to assist them. At many points throughout the text, we summarize the results of recent discussions or illustrative examples in tabular form to help students see the “big picture.” The basic ideas of chemical periodicity are introduced early (Chapters 4 and 5) and are used throughout the text. The simplified classification of acids and bases introduced in Chapter 6 is expanded in Chapter 10, after the appropriate background on structure and bonding has been provided. References are made to the classification of acids and bases and to the solubility guidelines throughout the text to emphasize the importance of systematizing and using previously covered information. Chapter 11 covers solution stoichiometry for both acid base and redox reactions, emphasizing the mole method.

After their excursion through gases and the kinetic–molecular theory (Chapter 12), liquids and solids (Chapter 13), and solutions (Chapter 14), students will have the appropriate background for a wide variety of laboratory experiments. These chapters also provide a strong presentation of the molecular basis of the physical behavior of matter.

Comprehensive chapters are presented on chemical thermodynamics (Chapter 15) and chemical kinetics (Chapter 16). The discussion of entropy includes the concepts of dispersal of energy and dispersal of matter (disorder). The distinction between the roles of standard and nonstandard Gibbs free-energy change in predicting reaction spontaneity is clearly discussed. Chapter 15 is structured so that the first nine sections, covering thermochemistry and bond energies, could be presented much earlier in the course. Chapter 16 provides an early and consistent emphasis on the experimental basis of kinetics.

These chapters provide the necessary background for a strong introduction to chemical equilibrium in Chapter 17. This is followed by three chapters on equilibria in aqueous solutions. A chapter on electrochemistry (Chapter 21) and nuclear chemistry (Chapter 22), completes the common core of the text.

Organic chemistry is discussed in Chapters 23 and 24. Chapter 23 presents the classes of organic compounds, their structures and nomenclature (with major emphasis on the principal functional groups), and some fundamental classes of organic reactions. Chapter 24 presents isomerism and geometries of organic molecules, selected specific types, and an introduction to biopolymers.

The last four chapters cover coordination compounds (Chapter 25), the chemistry and uses of metals (Chapters 26 and 27), and the chemistry, properties, and reactions of nonmetals and metalloids (Chapter 28). Throughout these chapters, we have been careful to include appropriate applications of the principles that have been developed in the first part of the textbook.

Eight additional chapters are included in *A Qualitative Analysis Supplement*. In Chapter 29, important properties of the metals of the cation groups are tabulated, their properties are discussed, the sources of the elements are listed, their metallurgies are described, and a few uses of each metal are given.

Chapter 30 is a detailed introduction to the laboratory procedures used in semimicro qualitative analysis.

Chapters 31 through 35 cover the analysis of the groups of cations. (Cations that create serious disposal problems are no longer included in the qualitative analysis chapters. Mercury, silver, lead, and most chromium cations have been removed.) Each chapter includes a discussion of the important oxidation states of the metals, an introduction to the analytical procedures, and comprehensive discussions of the chemistry of each cation group. Detailed laboratory instructions, set off in color, follow. Students are alerted to pitfalls in advance, and alternate confirmatory tests and “cleanup” procedures are described for troublesome cations. A set of exercises accompanies each chapter.

In Chapter 31, the traditional Group 1 has been replaced by the traditional Group 2A (minus lead). Traditional Group 2B (minus mercury) constitutes the first part of Chapter 32; then Groups 1 and 2 (traditional 2A + 2B minus lead and mercury) make up the last part of Chapter 32. Chapter 33 includes all of the usual Group 3 elements. Chapter 34 covers Group 4, and Chapter 35 discusses Group 5.

Chapter 36 contains a discussion of some of the more sophisticated ionic equilibria of qualitative analysis. The material is presented in a single chapter for the convenience of the instructor.

A Flexible Presentation

We have exerted great effort to make the presentation as flexible as possible to give instructors the freedom to choose the order in which they teach topics. Some examples follow:

1. As in previous editions, we have clearly delineated the parts of Chapter 15, *Chemical Thermodynamics*, that can easily be moved forward by instructors who want to cover thermochemistry (Sections 15-1 to 15-9) after stoichiometry (Chapters 2 and 3).
2. Chapter 6, *Some Types of Chemical Reactions*, systematizes chemical reaction types and relates them to the periodic table. Reactions are classified as (a) oxidation–reduction reactions, (b) combination reactions, (c) decomposition reactions, (d) displacement reactions, (e) metathesis reactions (two types), and (f) gas-formation reactions. If desired, the material in this chapter can be presented at any later point in the course.
3. Some instructors prefer to discuss gases (Chapter 12) after stoichiometry (Chapters 2 and 3). Chapter 12 can be moved to that position.
4. Chapter 4 (*The Structure of Atoms*), Chapter 5 (*Chemical Periodicity*), and Chapter 7 (*Chemical Bonding*) provide comprehensive coverage of these key topics. The introduction of bond energies and bond lengths at this stage provides the basis for a better understanding of chemical bonding.
5. As in earlier editions, *Molecular Structure and Covalent Bonding Theories* (Chapter 8) includes parallel comprehensive VSEPR and VB descriptions of simple molecules. This approach has been widely praised. However, some instructors prefer separate presentations of these theories of covalent bonding. The chapter has been carefully

organized into numbered subdivisions to accommodate these instructors; detailed suggestions are also included at the beginning of the chapter.

6. Chapter 9 (*Molecular Orbitals in Chemical Bonding*) is a “stand-alone chapter” that may be omitted or moved with no loss in continuity.
7. Chapter 10 (*Reactions in Aqueous Solutions I: Acids, Bases, and Salts*) and Chapter 11 (*Reactions in Aqueous Solutions II: Calculations*) include comprehensive discussions of acid–base and redox reactions in aqueous solutions and solution stoichiometry calculations for acid–base and redox reactions.

Supporting Materials

Please visit www.cengage.com/chemistry/whitten/chemistry10e for information about student and instructor resources for this test.



Acknowledgments

We continue to acknowledge the critical role played by our longtime friend and editor, the late John Vondeling, in the development and continued success of this book.

The list of other individuals who contributed to the evolution of this book is long indeed. First, we would express our appreciation to the professors who contributed so much to our scientific education: Professors Arnold Gilbert, M. L. Bryant, the late W. N. Pirkle and Alta Sproull, C. N. Jones, S. F. Clark, R. S. Drago (KWW); the late Dorothy Vaughn, the late David Harker, the late Calvin Vanderwerf, the late Ralph N. Adams, and Professors F. S. Rowland, A. Tulinsky, and William von E. Doering (RED); Professors R. O'Connor, the late G. L. Baker, W. B. Cook, the late G. J. Hunt, the late A. E. Martell, and the late M. Passer (MLP); and Professors Richard Eisenberg, the late F. Albert Cotton, the late John A. Osborn, and Dr. Jerry Unruh (GGS).

The staff at Cengage Learning contributed immeasurably to the evolution of this book. As Executive Editor, Lisa Lockwood provided the authors a guiding hand and unstinting support throughout an often hectic development and production schedule. Alyssa White, our Developmental Editor, coordinated innumerable details of manuscript preparation and submission, scheduling, and reviewer comments; we are especially grateful to Teresa Trego for her patience and for her many unseen contributions and expert guidance through the often shifting sands of the modern electronic editorial process. Her work as Content Project Manager for Cengage Learning and her skillful hand in weaving together the many threads of the production process helped us with the production schedule and contributed greatly to the appearance, consistency, and quality of the book. Jeremy Glover, our superb photo researcher, gathered many excellent photographs with ingenuity, persistence, and patience. As Project Managers for Graphic World, Rhoda Bontrager and Grace Onderlinde handled the countless details of the production process thoroughly and efficiently, and we appreciate their keen eye for detail. Graphic World, our copy editor did much to refine our presentation. As Art Director, Maria Epes oversaw the development and execution of high-quality design and artwork that enhance both the appearance and substance of the book. We also thank Liz Woods, Assistant Editor, for coordinating the preparation of the print ancillaries, and Jessica Wang, Editorial Assistant, who handled a myriad of other details of which we were happily unaware. Expert artwork by Greg Gambino of 2064 Design is a wonderful enrichment of this edition. His remarkable ability to convert our two-dimensional drafts into beautiful three-dimensional art never failed to impress us. Finally, Senior Media Editor Lisa Weber's editorial experience contributed greatly to the remarkable development and implementation of instructional media in support of this edition.

Our special thanks go to David Shinn; Merchant Marine Academy, NY, for his careful checking of the accuracy of the text and the end-of-chapter Exercises.

The end-of-chapter exercises were considerably improved by the careful checking and numerous suggestions of Wendy Keeney-Kennicutt (Texas A&M University) and Vickie Williamson (Texas A&M University).

Finally, we are deeply indebted to our families, Betty, Andy, and Kathryn Whitten; Sharon and Brian Davis, Angela Wampler, and Laura Kane; Sandy Peck, Molly Levine, and Marci Culp; Sally Hunter, Bruce Tandy (& family), George (Sr.), Jenifer, Ted, and Eric Stanley. They have supported us during the many years we have worked on this project. Their understanding, encouragement, and moral support have “kept us going.”

Reviewers of the Tenth Edition

The following individuals performed a pre-revision review of the tenth edition, and their valuable comments helped guide the development of this edition.

Alan Colen, Kansas City Kansas Community College
George Kaminski, Worcester Polytechnic Institute
Elbert Malone, South Carolina State University
Arnulfo Mar, UT-Brownsville
Mark Ott, Jackson Community College
John Paparelli, San Antonio College
Mary Leigh Poole, Holmes Community College
Edward Vickner, Gloucester Community College
Kazushige Yokoyama, SUN Geneseo College

Reviewers of the First Nine Editions of General Chemistry

Edwin Abbott, Montana State University; Ed Acheson, Millikin University; David R. Adams, North Shore Community College; Carolyn Albrecht; Steven Albrecht, Ball State University; Dolores Aquino, San Jacinto College Central; Ale Arrington, South Dakota School of Mines; George Atkinson, Syracuse University; Charles Atwood, University of Georgia; Jerry Atwood, University of Alabama; William G. Bailey, Broward Community College; Major Charles Bass, United States Military Academy; Shuhsien Wang Batamo, Houston Community College; J. M. Bellama, University of Maryland; Fereshteh Billiot, Texas A&M University at Corpus Christi; Carl B. Bishop, Clemson University; Muriel B. Bishop, Clemson University; James R. Blanton, The Citadel; George Bodner, Purdue University; Simon Bott, University of Houston; Fitzgerald B. Bramwell, University of Kentucky; Joseph Branch, Central Alabama Community College; Greg Brewer, The Citadel; Clark Bricker, University of Kansas; Robert Broman, University of Missouri; William Brown, Beloit College; Robert F. Bryan, University of Virginia; Barbara Burke, California State Polytechnic, Pomona; L. A. Burns, St. Clair County Community College; Julio F. Caballero, San Antonio College; James Carr, University of Nebraska, Lincoln; Elaine Carter, Los Angeles City College; Ann Cartwright, San Jacinto College Central; Thomas Cassen, University of North Carolina; Martin Chin, San Jose State University; Evelyn A. Clarke, Community College of Philadelphia; Kent Clinger, David Lipscomb University; Lawrence Conroy, University of Minnesota; Mark Cracolice, University of Montana; Julian Davies, University of Toledo; William M. Davis, University of Texas at Brownsville; Randall Davy, Liberty University; John DeKorte, Glendale Community College (Arizona); Mark Draganjac, Arkansas State University; George Eastland, Jr., Saginaw Valley State University; Harry Eick, Michigan State University; Mohammed El-Mikki, University of Toledo; Dale Ensor, Tennessee Technological University; Lawrence Epstein, University of Pittsburgh; Sandra Etheridge, Gulf Coast Community College; Darrell Eyman, University of Iowa; Nancy Faulk, Blinn College; Wade A. Freeman, University of Illinois, Chicago Circle; Mark Freilich, Memphis State University; Travis D. Fridgen, Wilfrid Laurier University; Richard Gaver, San Jose State University; Dr. Lucio Gelmini, Grant MacEwan College; Gary Gray, University of Alabama, Birmingham;

Robert Hanrahan, University of Florida; Marilyn Hart, Minnesota State University at Mankato; Alton Hassell, Baylor University; Jack D. Hefley, Blinn College–Bryan Campus; Henry Heikkinen, University of Maryland; Forrest C. Hentz, North Carolina State University; R. K. Hill, University of Georgia; Donna S. Hobbs, Augusta State University; Bruce Hoffman, Lewis and Clark College; Larry Houck, Memphis State University; Arthur Hufnagel, Erie Community College, North Campus; Wilbert Hutton, Iowa State University; Albert Jache, Marquette University; William Jensen, South Dakota State University; M. D. Joeston, Vanderbilt University; Stephen W. John, Lane Community College; Milton Johnston, University of South Florida; Andrew Jorgensen, University of Toledo; Margaret Kastner, Bucknell University; Wendy Keeney-Kennicutt, Texas A&M University; Philip Kinsey, University of Evansville; Leslie N. Kinsland, University of Southwestern Louisiana; Donald Kleinfelter, University of Memphis; Marlene Kolz; Bob Kowerski, College of San Mateo; Larry Krannich, University of Alabama, Birmingham; Peter Krieger, Palm Beach Community College; Charles Kriley, Grove City College; Charles Kriley, Purdue University, Calumet; James Krueger, Oregon State University; Norman Kulevsky, University of North Dakota; Robert Lamb, Ohio Northern University; Alfred Lee, City College of San Francisco; Patricia Lee, Bakersfield College; William Litchman, University of New Mexico; Ramon Lopez de la Vega, Florida International University; Joyce Maddox, Tennessee State University; Gilbert J. Mains, Oklahoma State University; Olivier Marcq, American University; Ronald Marks, Indiana University of Pennsylvania; William Masterton, University of Connecticut; Toni McCall, Angelina College; William E. McMullen, Texas A&M University; Rosalyn Meadows, Wallace State Community College; Clinton Medbery, The Citadel; Joyce Miller, San Jacinto College; Richard Mitchell, Arkansas State University; Stephanie Morris, Pellissippi State Technical Community College; Kathleen Murphy, Daemen College; Stephanie Myers, Augusta State University; Kathy Nabona, Austin Community College – Northridge; Joyce Neiburger, Purdue University; Deborah Nycz, Broward Community College; Barbara O'Brien, Texas A&M University; Brent Olive, University of North Alabama; Christopher Ott, Assumption College; Stephen J. Paddison, University of Alabama at Huntsville; James L. Pauley, Pittsburgh State University; John Phillips, Purdue University, Calumet; Richard A. Pierce, Jefferson College; William Pietro, University of Wisconsin, Madison; Ronald O. Ragsdale, University of Utah; Susan Raynor, Rutgers University; Scott W. Reeve, Arkansas State University; Randal Remmel; Gary F. Riley, St. Louis College of Pharmacy; Shashi Rishi, Greenville Technical College; Don Roach, Miami Dade Community College; Eugene Rochow, Harvard University; Jimmy R. Rogers, University of Texas at Arlington; Roland R. Roskos, University of Wisconsin, La Crosse; John Ruff, University of Georgia; George Schenk, Wayne State University; James M. Schlegel, Rutgers University, Newark; Mary Jane Schultz, Tufts University; William Scroggins, El Camino College; Curtis Sears, Georgia State University; Diane Sedney, George Washington University; Mahesh Sharma, Columbus College; Alka Shukla, Houston Community College; Shyam S. Shukla, Lamar University; Cheryl Snyder, Schoolcraft College; C. H. Stammer, University of Georgia; Yi- Noo Tang, Texas A&M University; John Thompson, Lane Community College; Margaret Tierney, Prince George's Community College; Henry Tracy, University of Southern Maine; Janice Turner, Augusta College; Cyriacus Chris Uzomba, Austin Community College–Rio Grande; James Valentini, University of California, Irvine; Douglas Vaughan; Victor Viola, Indiana University; W. H. Waggoner, University of Georgia; Mona Wahby, Macomb Community College; Thomas R. Webb, Auburn University; Susan Weiner, West Valley College; Donald Williams, Hope College; Vickie Williamson, Texas A&M University; David Winters, Tidewater Community College; Wendy S. Wolbach, Illinois Wesleyan University; Kevin L. Wolf, Texas A&M University; Marie Wolff, Joliet Junior College; James Wood, Palm Beach Community College; Robert Zellmer, Ohio State University; and Steve Zumdahl, University of Illinois.

Kenneth W. Whitten M. Larry Peck

Raymond E. Davis George G. Stanley

For the Student

We have written this text to assist you as you study chemistry. Chemistry is a fundamental science—some call it the central science. As you and your classmates pursue diverse career goals, you will find that the vocabulary and ideas presented in this text will be useful in more places and in more ways than you may imagine now. We begin with the most basic vocabulary and ideas. We then carefully develop increasingly sophisticated ideas that are necessary and useful in all the other physical sciences, the biological sciences, and the applied sciences such as medicine, dentistry, engineering, agriculture, and home economics.

We have made the early chapters as nearly self-contained as possible. The material can be presented in the order considered most appropriate by your professor. Some professors will cover chapters in a different sequence or will omit some chapters completely—the text was designed to accommodate this. Early in each section we have attempted to provide the experimental basis for the ideas we then develop. By “experimental basis” we mean the observations of and experiments on the phenomena that have been most important in developing concepts. We then present an explanation of the experimental observations.

Chemistry is an experimental science. We know what we know because we (literally thousands of scientists) have observed it to be true. Theories have been evolved to explain experimental observations (facts). Successful theories explain observations fully and accurately. More important, they enable us to predict the results of experiments that have not yet been performed. Thus, we should always keep in mind the fact that experiment and theory go hand in hand. They are intimately related parts of our attempt to understand and explain natural phenomena.

A word about the cover: Water is surely the most important substance on this planet. Its remarkable physical and chemical properties provide the very basis of all known forms of life, due to the substance’s ability to dissolve a huge variety of solutes and its remarkable acid/base characteristics. Most scientific “searches” for physical evidence of extraterrestrial life focus to a significant degree on evidence for the existence of liquid water. In this aspect, it is more important than oxygen—there are anaerobic life forms that don’t require oxygen, but none that do not need water. It is also the key to global climate and temperature control. Earth has the most moderate temperature range of the planets (an essential requirement for life as we know it), and this is mainly due to the very unusually high specific heat and other remarkable thermal properties of water. And each of these important properties, along with many other physical and chemical properties, is due to the *molecular structure* of water. We concluded that no other molecule could better highlight our emphasis on the relationship between molecular structure and chemical/physical properties.

“What is the best way to study chemistry?” is a question we are asked often by our students. While there is no single answer to this question, the following suggestions may be helpful. Your professor may provide additional suggestions. A number of supplementary materials accompany this text. All are designed to assist you as you study chemistry. Your professor may suggest that you use some of them.

Students often underestimate the importance of the act of writing as a tool for learning. Whenever you read, do not just highlight passages in the text, but also take notes. Whenever you work problems or answer questions, write yourself explanations of why each step was done or how you reasoned out the answer. In this way, you will develop the art of teaching yourself—which is the *real* goal of education. Keep a special section of your note-

book for working out problems or answering questions. The very act of writing forces you to concentrate more on what you are doing, and you learn more. This is true even if you never go back to review what you wrote earlier. Of course, these notes should also help you to review for an examination.

You should always read over the assigned material before it is covered in class. This helps you to recognize the ideas as your professor discusses them. Then take careful class notes. At the first opportunity, and certainly the same day, you should recopy your class notes. As you do this, fill in more details where you can. Try to work the illustrative examples that your professor solved in class without looking at the solutions in your notes. If you must look at the solutions, look at only one line (step), and then try to figure out the next step. Read the assigned material again and take notes, integrating these with your class notes. Reading should be much more informative the second time.

Review the “Key Terms” at the end of the chapter to be sure that you understand the meaning of each term. Work the illustrative examples in the text while covering the solutions with a sheet of paper. If you find it necessary to look at the solutions, look at only one line at a time and try to figure out the next step. Answers to illustrative examples are displayed on blue backgrounds. At the end of most examples, we suggest related questions from the end-of-chapter exercises. You should work these suggested exercises as you come to them. Make sure that you read the “Problem-Solving Tips” and the associated margin alerts (denoted “Stop & Think”); these will help you avoid common mistakes and understand more complex ideas.

This is a good time to work through the appropriate chapter in the *Study Guide to Chemistry*. This will help you to see an overview of the chapter, to set specific study goals, and then to check and improve your grasp of basic vocabulary, concepts, and skills. Next, work the assigned exercises at the end of the chapter.

The appendices contain much useful information. You should become familiar with them and their contents so that you may use them whenever necessary. Answers to selected even-numbered numerical exercises are given at the end of the text so that you may check your work.

The Internet is an increasingly important source of many kinds of information. The “Beyond the Textbook” problems at the end of each chapter ask you to make use of the Internet to find answers to these questions. Conceptual exercises develop your ability to apply your knowledge to relevant situations.

We heartily recommend the *Study Guide to Chemistry*, the *Student Solutions Manual*, and the *Lecture Outline*, all of which were written to accompany this text.

The *Study Guide to Chemistry* by Raymond E. Davis and James Petrich provides an overview of each chapter and emphasizes the threads of continuity that run through chemistry. It lists study goals, tells you which ideas are most important and why they are important, and provides many forward and backward references. Additionally, the *Study Guide* contains many easy to moderately difficult questions that test your understanding of basic concepts and skills and enable you to gauge your progress. These short questions provide excellent practice in preparing for examinations. Answers are provided for all questions, and many include explanations or references to appropriate sections in the text.

The *Student Solutions Manual* by Wendy Keeney-Kennicutt contains detailed solutions and answers to all even-numbered end-of-chapter exercises. It also has many helpful references to appropriate sections and illustrative examples in the text.

The *Lecture Outline* by Charles Atwood helps you organize material in the text and serves as a helpful classroom note-taking supplement so that you can pay more attention to the lecture.

Molecular Art

This edition places a great emphasis on molecular reasoning. This chemical reasoning is illustrated with extensive new molecular art, much of it computer-generated. Some examples of the ways in which molecular art is used in this edition include the following:

1. **Structures or reactions.** Molecular art is used to give a molecular-level view of a concept being discussed, as in the following interpretation of a balanced chemical equation.

Unless otherwise noted, all content on this page is © Cengage Learning.

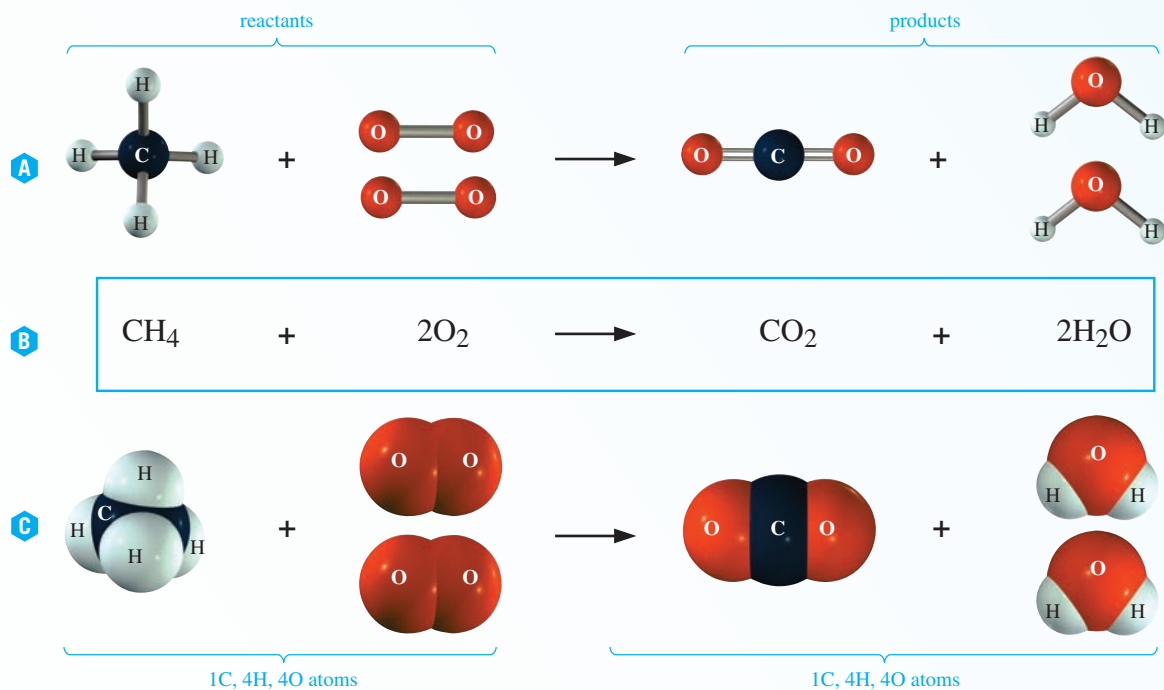


Figure 3-1 Three representations of the reaction of methane with oxygen to form carbon dioxide and water. Chemical bonds are broken and new ones are formed in each representation. Part (a) illustrates the reaction using ball-and-stick models, (b) uses chemical formulas, and (c) uses space-filling models.

Figure 1-7 compares the physical properties of three states of matter: solid, liquid, and gas, using iodine, bromine, and chlorine as examples.

(left) Iodine (I₂(s)): A solid element. The image shows a small amount of dark, crystalline iodine in a white dish. A magnifying glass shows a close-up of the solid iodine molecules, which are represented by purple spheres.

(center) Bromine (Br₂(ℓ)): A liquid element. The image shows a small amount of dark red liquid bromine in a glass flask. A magnifying glass shows a close-up of the liquid bromine molecules, which are represented by red spheres.

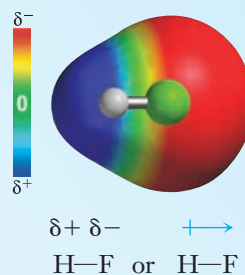
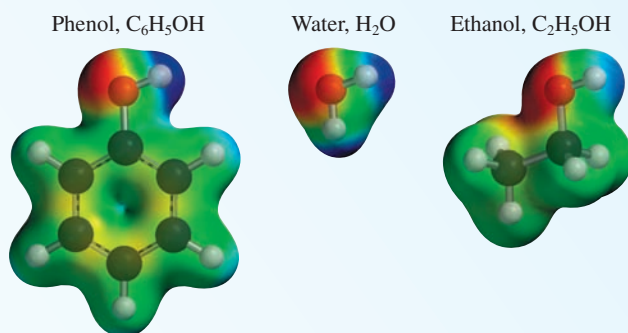
(right) Chlorine (Cl₂(g)): A gaseous element. The image shows a small amount of greenish-yellow gas chlorine in a glass flask. A magnifying glass shows a close-up of the gaseous chlorine molecules, which are represented by green spheres.

Property	Solid	Liquid	Gas
Rigidity	Rigid	Flows and assumes shape of container	Fills any container completely
Expansion on heating	Slight	Slight	Expands indefinitely
Compressibility	Slight	Slight	Highly compressible

Figure 1-7 A comparison of some physical properties of the three states of matter. (left) Iodine, a solid element. (center) Bromine, a liquid element. (right) Chlorine, a gaseous element.

2. **Macro–micro art.** Molecular art presented together with a photograph of a sample or an experiment clarifies the molecular behavior.
3. **Electrostatic charge potential (ECP) figures** that illustrate the charge density in molecules. Charge distributions within molecules are illustrated with colorful ECP figures. These will help you visualize their effects on molecular properties and intermolecular interactions. Color scales are now included to remind you that these plots range from red (most negative) through green (neutral) to blue (most positive).

Most of these ECP images have been updated with embedded ball-and-stick molecular models to more clearly indicate where the various charges reside. In the following figure, ethanol, water, and phenol are compared and the ECP surfaces show the increasing polarity of the O—H bond that corresponds to the increasing acidity of these compounds.



Keys for Color Codes

In addition to full-color photography and art, we have used color to help you identify and organize important ideas, techniques, and concepts as you study this book.

1. Important ideas, mathematical relationships, and summaries are displayed on light blue screens, spanning the width of the text.

There is no observable change in the quantity of matter during a chemical reaction or during a physical change.

2. Answers to examples are shown on light blue screens. Intermediate steps (logic, guidance, and so on) are shown on light tan screens.

EXAMPLE 1-9 English-Metric Conversion

Express 1.0 gallon in milliliters.

Plan

We ask $\underline{\hspace{1cm}}$ mL = 1.0 gal and multiply by the appropriate factors.

gallons $\rightarrow$ quarts $\rightarrow$ liters $\rightarrow$ milliliters

Solution

$$\underline{\hspace{1cm}} \text{ mL} = 1.0 \text{ gal} \times \frac{4 \text{ qt}}{1 \text{ gal}} \times \frac{1 \text{ L}}{1.06 \text{ qt}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 3.8 \times 10^3 \text{ mL}$$

You should now work Exercise 40.

3. Acidic and basic properties are contrasted by using blue and pink, respectively. These colors are based on the electrostatic charge potential surfaces where negative charge

Table 6-5 Bonding, Solubility, Electrolyte Characteristics, and Predominant Forms of Solutes in Contact with Water

	Acids		Bases			Salts	
	Strong Acids	Weak Acids	Strong Bases	Insoluble Bases	Weak Bases	Soluble Salts	Insoluble Salts
Examples	HCl HNO ₃	CH ₃ COOH HF	NaOH Ca(OH) ₂	Mg(OH) ₂ Al(OH) ₃	NH ₃ CH ₃ NH ₂	KCl, NaNO ₃ , NH ₄ Br	BaSO ₄ , AgCl, Ca ₃ (PO ₄) ₂
Pure compound ionic or molecular?	Molecular	Molecular	Ionic	Ionic	Molecular	Ionic	Ionic
Water-soluble or insoluble?	Soluble*	Soluble*	Soluble	Insoluble	Soluble†	Soluble	Insoluble
≈ 100% ionized or dissociated in dilute aqueous solution?	Yes	No	Yes	(footnote‡)	No	Yes§	(footnote‡)
Written in ionic equations as	Separate ions	Molecules	Separate ions	Complete formulas	Molecules	Separate ions	Complete formulas

*Most common inorganic acids and the low-molecular-weight organic acids (—COOH) are water-soluble.

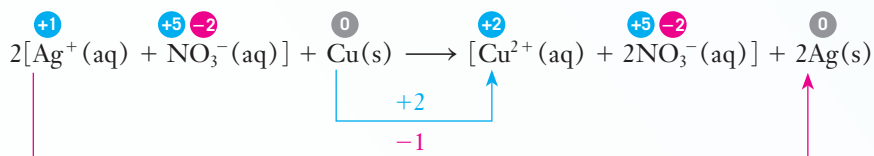
†The low-molecular-weight amines are water-soluble.

‡The *very small concentrations* of “insoluble” metal hydroxides and insoluble salts in saturated aqueous solutions are nearly completely dissociated.

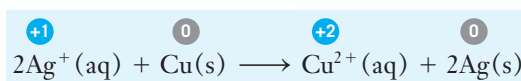
§There are a few exceptions. A few soluble salts are molecular (and not ionic) compounds.

is indicated by red and positive charge is indicated by blue. The most common acidic species is H⁺ and cationic, while all bases have lone pairs that have partial negative charge. Salts or neutral solutions are indicated in pale purple.

4. Red and blue are used in oxidation–reduction reactions and electrochemistry.
 - a. Oxidation numbers are shown in red circles for negative states, blue circles for positive states, and grey for neutral or elemental states. Oxidation is indicated by blue, and reduction is indicated by red.

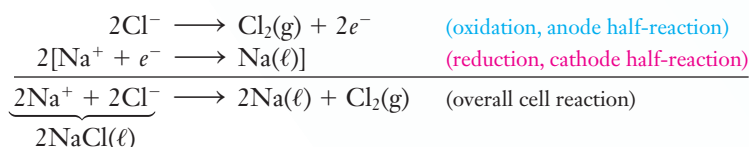


The nitrate ions, NO₃[−], are spectator ions. Canceling them from both sides gives the net ionic equation:

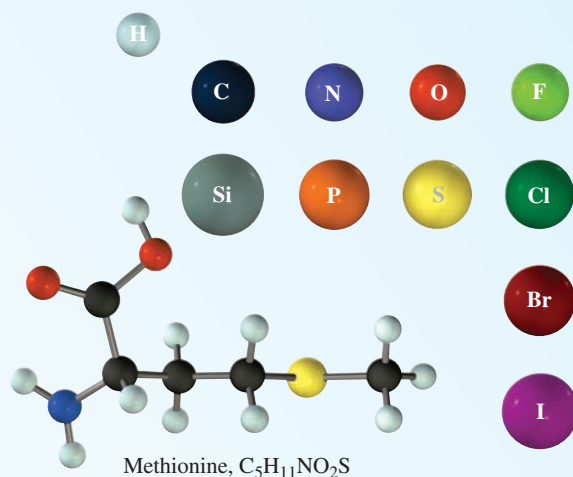


This is a redox equation. The oxidation number of silver decreases from +1 to zero; silver ion is reduced and is the oxidizing agent. The oxidation number of copper increases from zero to +2; copper is oxidized and is the reducing agent.

- b. In electrochemistry (Chapter 21), we learn that oxidation occurs at the *anode*; consistent with the colors just described, we use blue to indicate the anode and its half-reaction. Similarly, reduction occurs at the *cathode*, so we use red to indicate the cathode and its half-reaction.



5. The space-filling and ball-and-stick molecular models use a consistent color scheme for the following atom types (these parallel common organic usage).



6. Atomic orbitals are shown in blue (or blue and purple when we wish to emphasize phase differences).

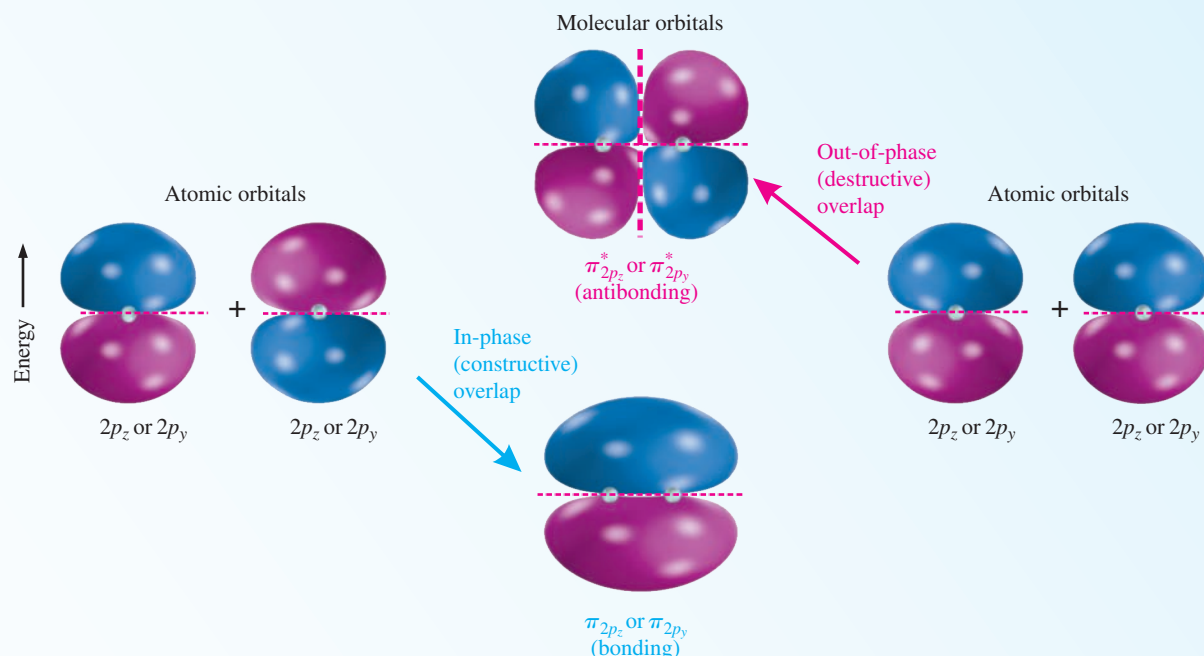
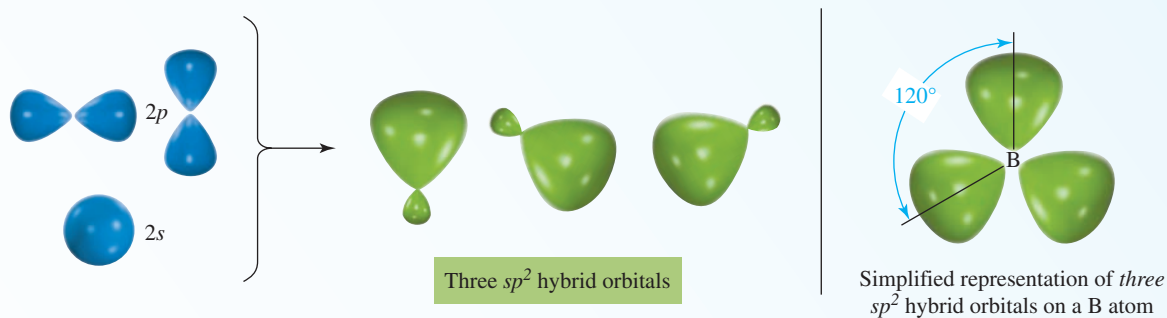


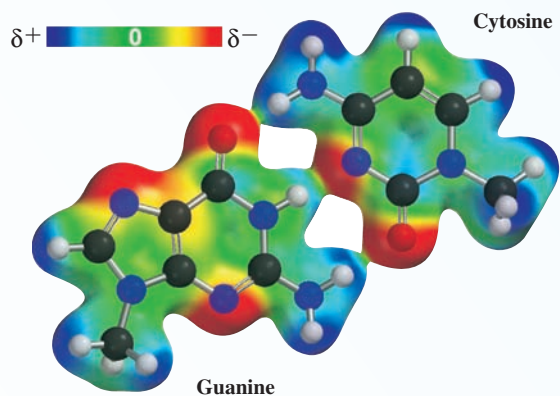
Figure 9-4 The π_{2p} and π_{2p}^* molecular orbitals from overlap of one pair of $2p$ atomic orbitals (for instance, $2p_y$ orbitals). There can be an identical pair of molecular orbitals at right angles to these, formed by another pair of p orbitals on the same two atoms (in this case, $2p_z$ orbitals).

7. Hybridization schemes and hybrid orbitals are emphasized in green.



Unless otherwise noted, all content on this page is © Cengage Learning.

8. Electrostatic charge potential (ECP) representations emphasize the distribution of charge in a molecule. In these drawings, the charge is shown on a color scale ranging from red (most negative) through green (neutral) to blue (most positive).



Hydrogen bonding between two DNA base pairs



9. Color-coded periodic tables emphasize the classification of the elements as metals (blue), nonmetals (tan), and metalloids (green). Please study the periodic table inside the front cover carefully so that you recognize this color scheme.

The Foundations of Chemistry

1



Chemistry is everywhere! From the combustion of wood to the synthetic fibers that make up much of our clothing. The steel cooking grate is an alloy of iron and carbon (and if it is stainless steel it has other metals such as chromium and nickel mixed in). The plants in the background use a remarkable photochemical reaction to convert CO_2 and water into complex carbohydrates. Our bodies are filled with both inorganic and bioorganic compounds such as bone and proteins, and run on a myriad of chemical reactions needed to keep us alive. Construction materials are made from both natural and recycled sources. Aluminum has many uses, based on its low density and its resistance to corrosion. Heat from a fire can cook food as well as cause skin damage. Clouds consist of tiny droplets of water formed by condensation of water vapor.

oliveromg/Shutterstock.com

OUTLINE

- 1-1 Matter and Energy
- 1-2 Chemistry—A Molecular View of Matter
- 1-3 States of Matter
- 1-4 Chemical and Physical Properties
- 1-5 Chemical and Physical Changes
- 1-6 Mixtures, Substances, Compounds, and Elements
- 1-7 Measurements in Chemistry
- 1-8 Units of Measurement
- 1-9 The Unit Factor Method (Dimensional Analysis)
- 1-10 Percentage
- 1-11 Density and Specific Gravity
- 1-12 Heat and Temperature
- 1-13 Heat Transfer and the Measurement of Heat

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Use the basic vocabulary of matter and energy
- ▶ Recognize models of selected atoms and molecules
- ▶ Distinguish between chemical and physical properties and between chemical and physical changes
- ▶ Recognize various forms of matter: homogeneous and heterogeneous mixtures, substances, compounds, and elements and their molecular representations
- ▶ Apply the concept of significant figures
- ▶ Apply appropriate units to describe the results of measurement
- ▶ Use the unit factor method to carry out conversions among units
- ▶ Describe temperature measurements on various common scales, and convert between these scales
- ▶ Carry out calculations relating temperature change to heat gained or lost

Thousands of practical questions are studied by chemists. A few of them are

How can we modify a useful drug so as to improve its effectiveness while minimizing any harmful or unpleasant side effects?

How can we develop better materials to be used as synthetic organs for replacement surgery?

Which substances could help to prevent rejection of foreign tissue in organ transplants?

What improvements in fertilizers or pesticides can increase agricultural yields? How can this be done with minimal environmental danger?

How can we get the maximum work from a fuel while producing the least harmful emissions possible?

Which really poses the greater environmental threat—the burning of fossil fuels and the resulting contribution to the greenhouse effect and climatic change, or the use of nuclear power and the related radiation and disposal problems?

How can we develop suitable materials for the semiconductor and microelectronics industry? Can we develop a battery that is cheaper, lighter, and more powerful?

What changes in structural materials could help to make aircraft lighter and more economical, yet at the same time stronger and safer?

What relationship is there between the substances we eat, drink, or breathe and the possibility of developing cancer? How can we develop substances that are effective in killing cancer cells preferentially over normal cells?

Can we economically produce fresh water from seawater for irrigation or consumption?

How can we slow down unfavorable reactions, such as the corrosion of metals, while speeding up favorable ones, such as the growth of foodstuffs?

Chemistry touches almost every aspect of our lives, our culture, and our environment. Its scope encompasses the air we breathe, the food we eat, the fluids we drink, the clothing we wear, the dwellings we live in, and the transportation and fuel supplies we use, as well as our fellow creatures.

Chemistry is the science that describes matter—its properties, the changes it undergoes, and the energy changes that accompany those processes.

Matter includes everything that is tangible, from our bodies and the stuff of our everyday lives to the grandest objects in the universe. Some call chemistry the central



Irina Pestova/Shutterstock.com

Enormous numbers of chemical reactions are necessary to produce a human being.

science. It rests on the foundation of mathematics and physics and in turn underlies the life sciences—biology and medicine. To understand living systems fully, we must first understand the chemical reactions and the factors that control and affect them. The chemicals in our bodies profoundly affect even the personal world of our thoughts and emotions.

No one can be expert in all aspects of such a broad science as chemistry. Sometimes we arbitrarily divide the study of chemistry into various branches. Of all the elements, carbon is the most versatile in its bonding. It is a key element in many substances that are essential to life. All forms of living matter contain compounds with carbon combined with hydrogen and sometimes with a few other elements such as oxygen, nitrogen, and sulfur. **Organic chemistry** is the study of all such compounds. **Inorganic chemistry** is the study of all other compounds, but also includes some of the simpler carbon-containing compounds such as carbon monoxide, carbon dioxide, carbonates, and bicarbonates. In the early days of chemistry, living matter and inanimate matter were believed to be entirely different. We now know that many of the compounds found in living matter can be made from nonliving, or “inorganic,” sources. Thus, the terms “organic” and “inorganic” have different meanings than they did originally. The branch of chemistry that is concerned with the detection or identification of substances present in a sample (*qualitative analysis*) or with the amount of each substance that is present (*quantitative analysis*) is called **analytical chemistry**. **Physical chemistry** applies the mathematical theories and methods of physics to the properties of matter and to the study of chemical processes and their accompanying energy changes. As its name suggests, **biochemistry** is the study of the chemistry of processes in living organisms. Such divisions are arbitrary, and most chemical studies involve more than one of these traditional areas of chemistry. The principles you will learn in a general chemistry course are the foundation of all branches of chemistry.

We understand simple chemical systems well. They lie near chemistry’s fuzzy boundary with physics, so they can often be described quite well by mathematical equations. We fare less well with more complicated systems. Even where our understanding is fairly thorough, we must make approximations, and often our knowledge is far from complete. Each year researchers provide new insights into the nature of matter and its interactions. Our scientific knowledge has been described as an expanding sphere that, as it grows, encounters an ever-enlarging frontier.

In our search for understanding, we must ask fundamental questions, such as:

How do substances combine to form other substances? How much energy is involved in changes that we observe?

How is matter constructed in its intimate detail? How are atoms and the ways that they combine related to properties that we can measure, such as color, hardness, chemical reactivity, and electrical conductivity?

What fundamental factors influence the stability of a substance? How can we force a desired (but energetically unfavorable) change to take place? What factors control the rate at which a chemical change takes place?

In your study of chemistry, you will learn about these and many other basic ideas that chemists have developed to help them describe and understand the behavior of matter. Along the way, we hope that you come to appreciate the development of this science, one of the grandest intellectual achievements of human endeavor. You will also learn how to apply these fundamental principles to solve real problems. One of your major goals in the study of chemistry should be to develop the ability to think critically and to solve problems (not just do numerical calculations!). In other words, you need to learn to manipulate not only numbers, but also ideas, words, and concepts.

In this chapter, our main goals are (1) to begin to get an idea of what chemistry is about and the ways in which chemists view and describe the material world and (2) to acquire some skills that are useful and necessary in the understanding of chemistry, its contribution to science and engineering, and its role in our daily lives.

► Lithium ions, for example, are effective in the treatment of some manic-depressive disorders.

1-1 Matter and Energy

► We might say that we can “touch” air when it blows in our faces, but we depend on other evidence to show that a still body of air fits our definition of matter.

► The term “kinetic” comes from the Greek word *kinein*, meaning “to move.” The word “cinema” is derived from the same Greek word.

► Nuclear energy is an important kind of potential energy.

Matter is anything that has mass and occupies space. **Mass** is a measure of the quantity of matter in a sample of any material. The more massive an object is, the more force is needed to put it in motion. All bodies consist of matter. Our senses of sight and touch usually tell us that an object occupies space. In the case of colorless, odorless, tasteless gases (such as air), our senses may fail us.

Energy is defined as the capacity to do work or to transfer heat. We are familiar with many forms of energy, including mechanical energy, light energy, electrical energy, and heat energy. Light energy from the sun is used by plants as they grow, electrical energy allows us to light a room by flicking a switch, and heat energy cooks our food and warms our homes. Energy can be classified into two principal types: kinetic energy and potential energy.

A body in motion, such as a rolling boulder, possesses energy because of its motion. Such energy is called **kinetic energy**. Kinetic energy represents the capacity for doing work directly. It is easily transferred between objects. **Potential energy** is the energy an object possesses because of its position, condition, or composition. Coal, for example, possesses chemical energy, a form of potential energy, because of its composition. Many electrical generating plants burn coal, producing heat, which is converted to electrical energy. A boulder located atop a mountain possesses potential energy because of its height and the presence of gravity. It can roll down the mountainside and convert its potential energy into kinetic energy.

We discuss energy because all chemical processes are accompanied by energy changes. As some processes occur, energy is released to the surroundings, usually as heat energy. We call such processes **exothermic**. Any combustion (burning) reaction is exothermic. Some chemical reactions and physical changes, however, are **endothermic**; that is, they absorb energy from their surroundings. An example of a physical change that is endothermic is the melting of ice.

The Law of Conservation of Matter

When we burn a sample of metallic magnesium in oxygen, the magnesium combines with the oxygen (Figure 1-1) to form magnesium oxide, a white powder. This chemical reaction is accompanied by the release of large amounts of energy in the form of heat and light. When we weigh the product of the reaction, magnesium oxide, we find that it is heavier than the original piece of magnesium. The increase in the mass of the solid is due to the combination of oxygen with magnesium to form magnesium oxide. Many experiments have shown that the mass of the magnesium oxide is exactly the sum of the masses of magnesium and oxygen that combined to form it. Similar statements can be made for all chemical reactions. These observations are summarized in the **Law of Conservation of Matter**:

There is no observable change in the quantity of matter during a chemical reaction or during a physical change.

This statement is an example of a **scientific (natural) law**, a general statement based on the observed behavior of matter to which no exceptions are known. A nuclear reaction, in which mass is converted into energy, or sometimes energy into mass, is *not* a chemical reaction.

The Law of Conservation of Energy

In exothermic chemical reactions, *chemical energy* is usually converted into *heat energy*. Some exothermic processes involve other kinds of energy changes. For example, some liberate light energy without heat, and others produce electrical energy without heat or light. In *endothermic* reactions, heat energy, light energy, or electrical energy is converted into chemical energy. Although chemical changes always involve energy changes, some energy transformations do not involve chemical changes at all. For example, heat energy may be converted into electrical energy or into mechanical energy without any simultane-



Charles D. Winters

Figure 1-1 Magnesium burns in oxygen to form magnesium oxide, a white solid. The mass of magnesium oxide formed is equal to the sum of the masses of oxygen and magnesium that formed it.

Unless otherwise noted, all content on this page is © Cengage Learning.

ous chemical changes. Many experiments have demonstrated that all the energy involved in any chemical or physical change appears in some form after the change. These observations are summarized in the **Law of Conservation of Energy**:

Energy cannot be created or destroyed in a chemical reaction or in a physical change. It can only be converted from one form to another.

The Law of Conservation of Matter and Energy

With the dawn of the nuclear age in the 1940s, scientists, and then the world, became aware that matter can be converted into energy. In nuclear reactions (Chapter 22), matter is transformed into energy. The relationship between matter and energy is given by Albert Einstein's now famous equation

$$E = mc^2$$

This equation says that the amount of energy released when matter is transformed into energy is the mass of matter transformed times the speed of light squared. Even a hydrogen bomb converts only a small amount of matter into energy. At the present time, we have not (knowingly) observed the transformation of energy into matter on a large scale. Matter-to-energy conversions do happen frequently on an extremely small scale in “atom smashers” (particle accelerators) used to induce nuclear reactions. Now that the equivalence of matter and energy is recognized, the **Law of Conservation of Matter and Energy** can be stated in a single sentence:

The combined amount of matter and energy available in the universe is fixed.

► Electricity is produced in hydroelectric plants by the conversion of mechanical energy (from flowing water) into electrical energy.

► Einstein formulated this equation in 1905 as a part of his theory of relativity. Its validity was demonstrated in 1939 with the first controlled nuclear reaction.

1-2 Chemistry—A Molecular View of Matter

The tremendous variety of matter present in our world consists of combinations of only about 100 basic substances called *elements*. Our everyday experiences with matter take place at the **macroscale**, that is, dealing with samples of matter of a size that we can see, handle, and manipulate. But the basic building blocks of matter are atoms and molecules, which make up elements and compounds. In our interactions with matter, we do not handle or typically observe these exceedingly tiny individual particles. Atoms and molecules exist at the **nanoscale**. (The general meaning of the prefix “nano” is *exceedingly small*; as we shall see later in this chapter, it has a definite numerical meaning of *one-billionth of*.) The chemical view of nature is that everything in the world around us is made up of atoms combined in very definite ways. Most substances are made up of small units called *molecules*. All of the properties and behavior of matter result from the properties of their atoms and molecules and the ways that they interact with one another. Throughout our study of chemistry, we always try to relate our macroscopic observations of matter to the nanoscale properties and behavior of its constituent atoms and molecules. Understanding these relationships is the very essence of chemistry; it provides us with a powerful way to describe the world around us and with the hope of exercising some responsible control over it as we seek answers to questions such as those that opened this chapter.

Throughout this book, we will study atoms and molecules in much more detail. For now, let's look at some of the basic ways that chemists represent and think about these important particles.

The Greek philosopher Democritus (470–400 BC) suggested that all matter is composed of tiny, discrete, indivisible particles that he called *atoms*. His ideas, based entirely on philosophical speculation rather than experimental evidence, were rejected for 2000 years. By the late 1700s, scientists began to realize that the concept of atoms provided an explanation for many experimental observations about the nature of matter.

By the early 1800s, the Law of Conservation of Matter (see Section 1-1) and the Law of Definite Proportions (see Section 1-6) were both accepted as general descriptions of how

STOP & THINK

One nanometer, nm, is equivalent to 10 angstroms, Å, a unit commonly used for atomic distances. All atoms and many small molecules are less than 1 nm in size and are, therefore, subnano.

► The term “atom” comes from the Greek language and means “not divided” or “indivisible.” We now know that atoms are “divisible” and are composed of smaller subatomic particles.

Unless otherwise noted, all content on this page is © Cengage Learning.

matter behaves. John Dalton (1766–1844), an English schoolteacher, tried to explain why matter behaves in such systematic ways as those expressed here. In 1808, he published the first “modern” ideas about the existence and nature of atoms. Dalton’s explanation summarized and expanded the nebulous concepts of early philosophers and scientists; more importantly, his ideas were based on *reproducible experimental results* of measurements by many scientists. These ideas form the core of **Dalton’s Atomic Theory**, one of the highlights in the history of scientific thought. In condensed form, Dalton’s ideas may be stated as follows:

► The radius of a calcium atom is only 0.000 000 019 7 cm, and its mass is 0.000 000 000 000 000 000 066 6 g. Later in this chapter, we will learn a better way to represent these numbers.

1. An element is composed of extremely small, indivisible particles called *atoms*.
2. All atoms of a given element have identical properties that differ from those of other elements.
3. Atoms cannot be created, destroyed, or transformed into atoms of another element via chemical or physical changes.
4. Compounds are formed when atoms of different elements combine with one another in small whole-number ratios.
5. The relative numbers and kinds of atoms are constant in a given compound.

Dalton believed that atoms were solid, indivisible spheres, an idea we now reject. But he showed remarkable insight into the nature of matter and its interactions. Some of his ideas could not be verified (or refuted) experimentally at the time. They were based on the limited experimental observations of his day. Even with their shortcomings, Dalton’s ideas provided a framework that could be modified and expanded by later scientists. Thus John Dalton is often considered to be the father of modern atomic theory.

The smallest particle of an element that maintains its chemical identity through all chemical and physical changes is called an **atom** (Figure 1-2). In Chapter 4, we will study the structure of the atom in detail; let us simply summarize here the main features of atomic composition. Atoms, and therefore *all* matter, consist principally of three **fundamental particles**: *electrons*, *protons*, and *neutrons*. These are the basic building blocks of atoms. The masses and charges of the three fundamental particles are shown in Table 1-1. The masses of protons and neutrons are nearly equal, but the mass of an electron is much smaller. Neutrons carry no charge. The charge on a proton is equal in magnitude, but opposite in sign, to the charge on an electron. Because any atom is electrically neutral it contains an equal number of electrons and protons.

The **atomic number** (symbol is *Z*) of an element is defined as the number of protons in the nucleus. In the periodic table, elements are arranged in order of increasing atomic numbers. These are the red numbers above the symbols for the elements in the periodic table on the inside front cover. For example, the atomic number of silver is 47.

A **molecule** is the smallest particle of an element or compound that can have a stable independent existence. In nearly all molecules, two or more atoms are bonded together in very small, discrete units (particles) that are electrically neutral.

47 ← atomic number
Ag ← symbol

► For the elements in column 8A, the noble gases, a molecule contains only one atom, so an atom and a molecule are the same (see Figure 1-2).

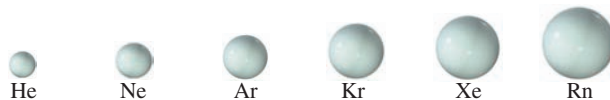


Figure 1-2 Relative sizes for atoms of the noble gases.

Table 1-1 Fundamental Particles of Matter

Particle (symbol)	Approximate Mass (amu)*	Charge (relative scale)
electron (e^-)	0.0	1–
proton (p or p^+)	1.0	1+
neutron (n or n^0)	1.0	none

* 1 amu = 1.6605×10^{-24} g.

Individual oxygen atoms, for example, are not stable at room temperature and atmospheric pressure. At these conditions, atoms of oxygen quickly combine to form pairs connected by chemical bonds. The oxygen with which we are all familiar is made up of two atoms of oxygen; it is a *diatomic* molecule with the formula O_2 . Hydrogen, nitrogen, fluorine, chlorine, bromine, and iodine are other examples of diatomic molecules (Figure 1-3).

Some other elements exist as more complex molecules. One form of phosphorus molecules consists of four atoms, and sulfur exists as eight-atom ring-shaped molecules at ordinary temperatures and pressures. Molecules that contain two or more atoms are called *polyatomic* molecules (Figure 1-4).

In modern terminology, O_2 is named dioxygen, H_2 is dihydrogen, P_4 is tetraphosphorus, and so on. Even though such terminology is officially preferred, it has not yet gained wide acceptance. Most chemists still refer to O_2 as oxygen, H_2 as hydrogen, P_4 as phosphorus, and so on.

Molecules of compounds are composed of more than one kind of atom in a definite ratio. A water molecule consists of two atoms of hydrogen and one atom of oxygen. A molecule of methane consists of one carbon atom and four hydrogen atoms. The shapes of a few molecules are shown in Figure 1-5 as ball-and-stick models.

► You should remember the common elements that exist as diatomic molecules: H_2 , N_2 , O_2 , F_2 , Cl_2 , Br_2 , I_2 .

Some common prefixes:

di = two
tri = three
tetra = four
penta = five
hexa = six
poly = more than one

► Methane, CH_4 , is the principal component of natural gas.

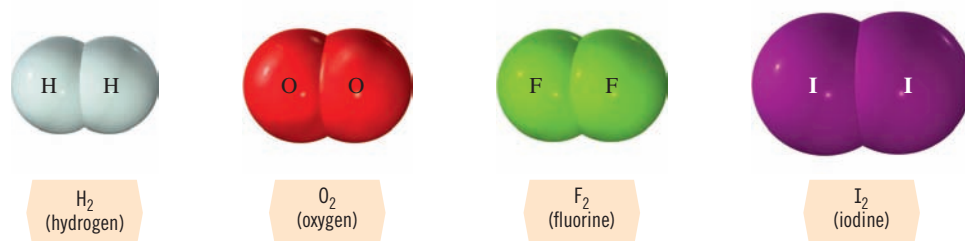


Figure 1-3 Models of diatomic molecules of some elements, approximately to scale. These are called *space-filling models* because they show the atoms with their approximate relative sizes.

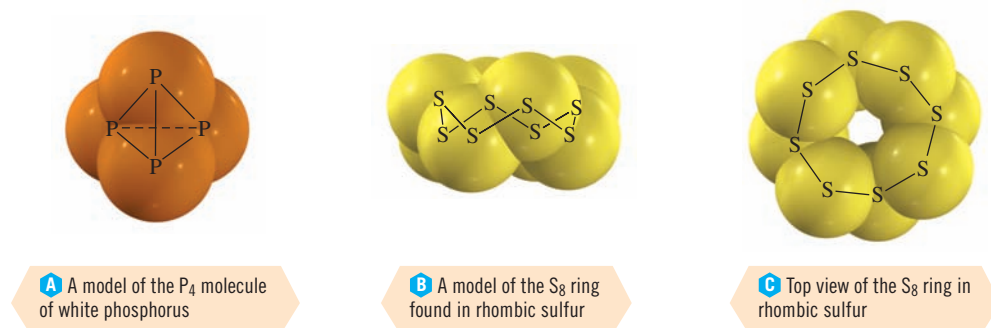


Figure 1-4 Space-filling models of some polyatomic elements.

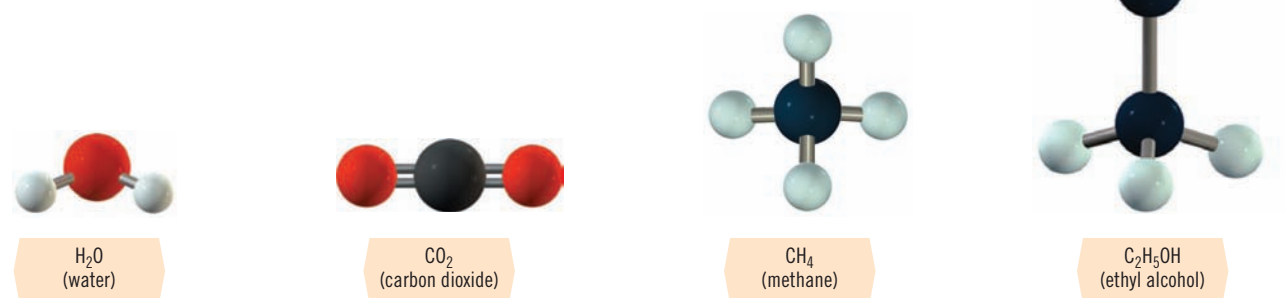


Figure 1-5 Formulas and ball-and-stick models for molecules of some compounds. Ball-and-stick models represent the atoms as smaller spheres than in space-filling models, in order to show the chemical bonds between the atoms as “sticks.” Single “sticks” between atoms represent single bonds, two sticks represent double bonds, three sticks represent triple bonds, etc.

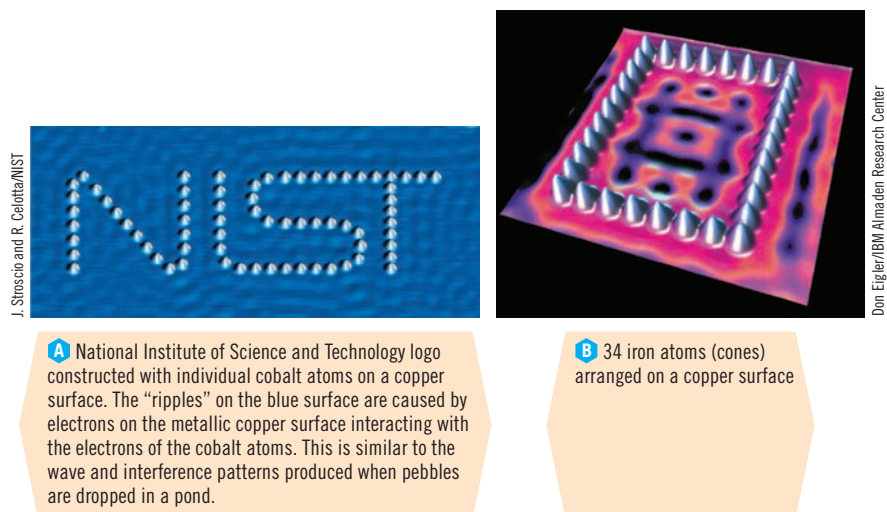


Figure 1-6

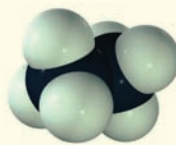
Atoms are the building blocks of molecules, and molecules are the stable forms of many elements and compounds. We are able to study samples of compounds and elements that consist of large numbers of atoms and molecules. With the scanning probe microscope it is now possible to “see” atoms (Figure 1-6). It would take millions of atoms to make a row as long as the diameter of the period at the end of this sentence.

EXAMPLE 1-1 Models

Look at each of the following models:



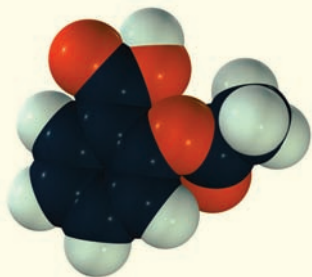
(i) krypton



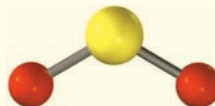
(ii) ethane



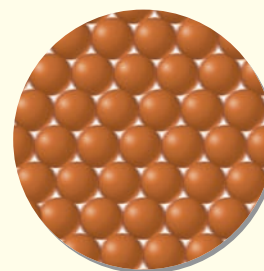
(iii) nitrogen



(iv) aspirin



(v) sulfur dioxide



(vi) copper

- Which of these models represents an atom?
- Which of these models represents a molecule?
- Which of these models represents an element?
- Which of these models represents a compound?

Plan

We use the descriptions of atoms, molecules, elements, and compounds given earlier in this section.

Solution

- (a) An atom is the smallest particle of an element. Only model i represents a single atom.
- (b) A molecule can be a single stable atom of an element or it can consist of a definite number of atoms (the same or different). Models i, ii, iii, iv, and v represent molecules.
- (c) An element contains a single kind of atom. Models i, iii, and vi represent elements.
- (d) A compound contains atoms of two or more different elements. Models ii, iv, and v represent compounds.

You should now work Exercise 18.

► With many examples we suggest selected exercises from the end of the chapter. These exercises use the skills or concepts from that example.

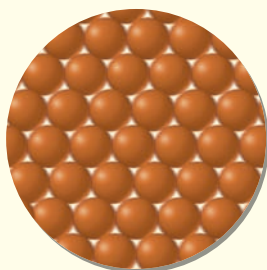
1-3 States of Matter

Matter can be classified into three states (Figure 1-7), although we might think of examples that do not fit neatly into any of the three categories. In the **solid** state, substances are rigid and have definite shapes. Volumes of solids do not vary much with changes in temperature and pressure. In crystalline solids, the individual particles that make up the solid occupy definite positions in the crystal structure. The strengths of interaction between the individual particles determine how hard and how strong the crystals are. In the **liquid** state, the individual particles are confined to a given volume. A liquid flows and assumes the shape of its container up to the volume of the liquid because the molecules are randomly oriented and have weaker forces of attraction between them relative to solids.

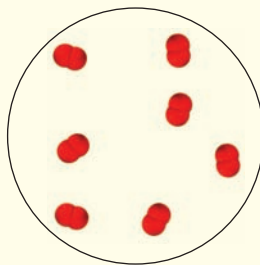
► We often represent the physical state of a substance with notations in parenthesis: (g) for gases, (ℓ) for liquids, (s) for solids.

EXAMPLE 1-2 Models

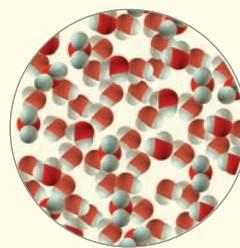
Identify the state of matter represented by each of the following models.



(a)



(b)



(c)

Plan

In a solid, the molecules are held close together in a regular arrangement. In a liquid, the molecules are close together but are randomly arranged because they flow past one another. In a gas, molecules are far apart.

Solution

- (a) The atoms are close together and regularly arranged, so this model represents the surface of a solid.
- (b) The molecules are far apart, so this model represents a gas.
- (c) The molecules are close together but randomly arranged, so this model represents a liquid.

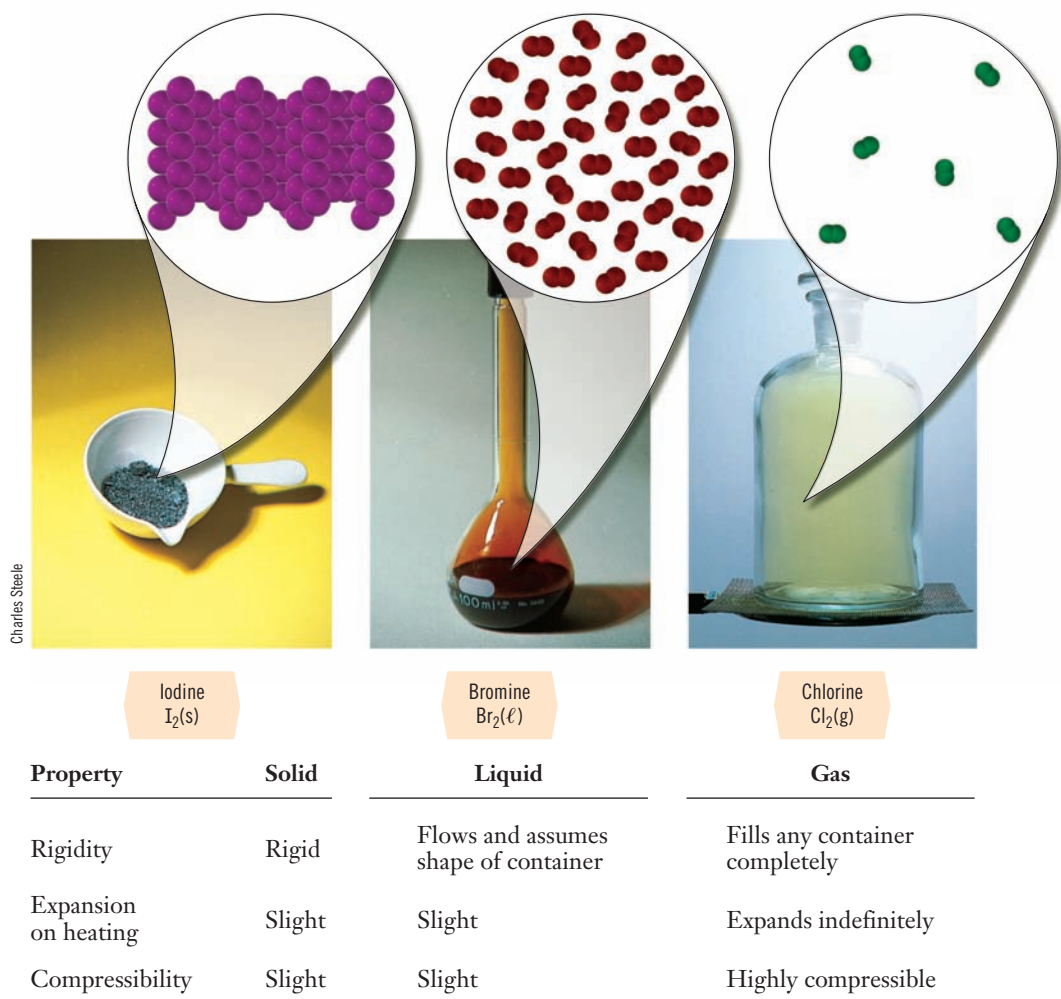


Figure 1-7 A comparison of some physical properties of the three states of matter. (left) Iodine, a solid element. (center) Bromine, a liquid element. (right) Chlorine, a gaseous element.

Liquids are very hard to compress because their molecules are very close together. **Gases** are much less dense than liquids and solids. A gas occupies all parts of any vessel in which it is confined. Gases are capable of indefinite expansion and are highly compressible. We conclude that gases consist primarily of empty space, meaning that the individual particles are quite far apart.

1-4 Chemical and Physical Properties

► The properties of a person include height, weight, sex, skin and hair color, and the many subtle features that constitute that person's general appearance.

To distinguish among samples of different kinds of matter, we determine and compare their **properties**. We recognize different kinds of matter by their properties. We can broadly classify these into chemical properties and physical properties.

Chemical properties are exhibited by matter as it undergoes changes in composition. These properties of substances are related to the kinds of chemical changes that the substances undergo. For instance, we have already described the combination of metallic magnesium with gaseous oxygen to form magnesium oxide, a white powder. A chemical property of magnesium is that it can combine with oxygen, releasing energy in the process. A chemical property of oxygen is that it can combine with magnesium.

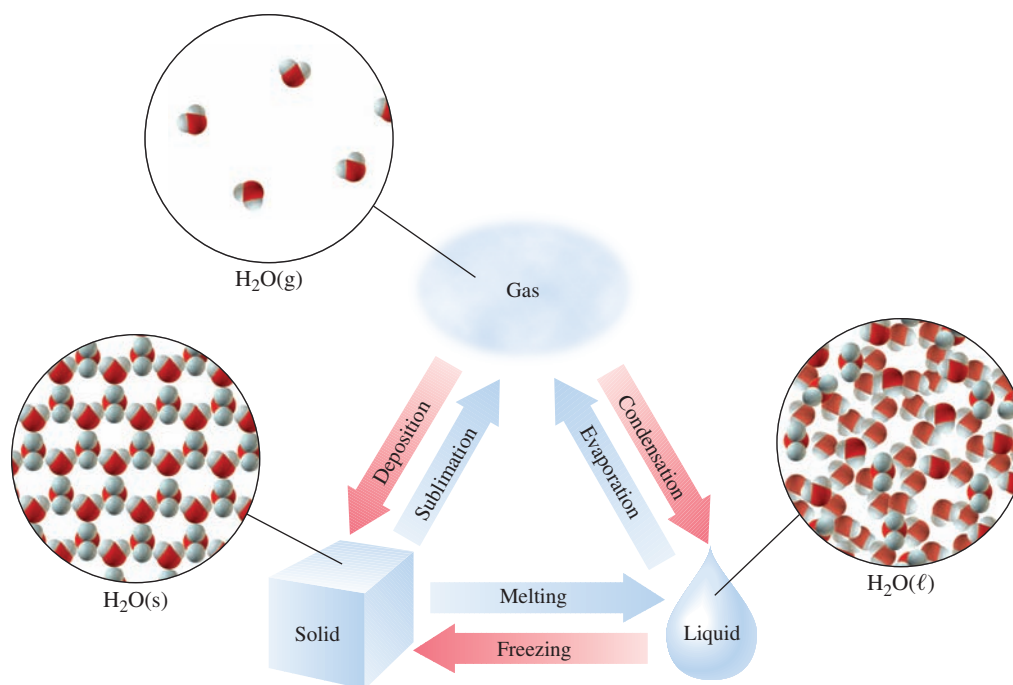


Figure 1-8 Physical changes that occur among the three states of matter. *Sublimation* is the conversion of a solid directly to a gas without passing through the liquid state; the reverse of that process is called *deposition*. The changes shown in blue are endothermic (absorb heat); those shown in red are exothermic (release heat). Water is a substance that is familiar to us in all three physical states. Molecules are close together in a solid and a liquid but far apart in a gas. The molecules in the solid are relatively fixed in position, but those in the liquid and gas can flow around each other.

All substances also exhibit **physical properties** that can be observed in the *absence of any change in composition*. Color, density, hardness, melting point, boiling point, and electrical and thermal conductivities are physical properties. Some physical properties of a substance depend on the conditions, such as temperature and pressure, under which they are measured. For instance, water is a solid (ice) at low temperatures but is a liquid at higher temperatures. At still higher temperatures, it is a gas (steam). As water is converted from one state to another, its composition is constant. Its chemical properties change very little. On the other hand, the physical properties of ice, liquid water, and steam are very different (Figure 1-8).

Properties of matter can be further classified according to whether they depend on the *amount* of substance present. The volume and the mass of a sample depend on (and are directly proportional to) the amount of matter in that sample. Such properties, which depend on the amount of material examined, are called **extensive properties**. By contrast, the color and the melting point of a substance are the same for a small sample as for a large one. Properties such as these are independent of the amount of material examined; they are called **intensive properties**. All chemical properties are intensive properties.

Because no two different substances have identical sets of chemical and physical properties under the same conditions, we can identify and distinguish among different substances. For instance, water is the only clear, colorless liquid that freezes at 0°C , boils at 100°C at one atmosphere of pressure, dissolves a wide variety of substances (e.g., copper(II) sulfate), and reacts violently with sodium (Figure 1-9). Table 1-2 compares several physical properties of a few substances. A sample of any of these substances can be distinguished from the others by observing their properties.

► Many compilations of chemical and physical properties of matter can be found on the internet. One site is maintained by the U.S. National Institute of Standards and Technology (NIST) at webbook.nist.gov. Perhaps you can find other sites.

► *One atmosphere* of pressure is the average atmospheric pressure at sea level.

Unless otherwise noted, all content on this page is © Cengage Learning.

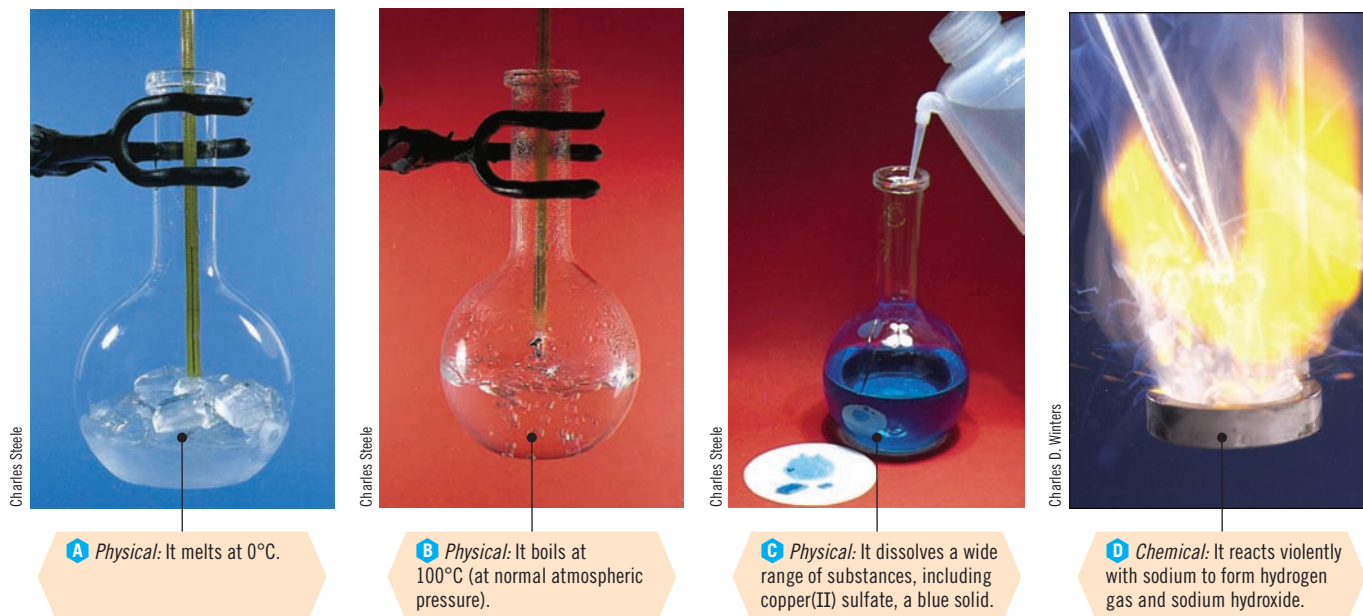


Figure 1-9 Some physical and chemical properties of water.

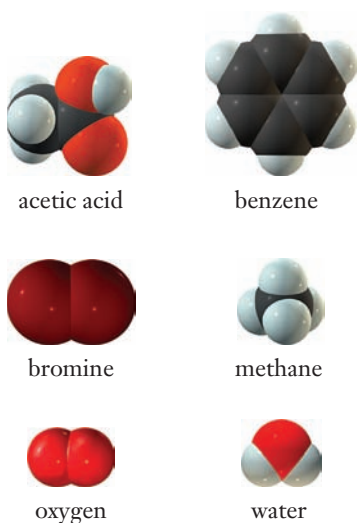


Table 1-2 Physical Properties of a Few Common Substances (at 1 atm pressure)

Substance	Melting Point (°C)	Boiling Point (°C)	Solubility at 25° C (g/100 g)		Density (g/cm ³)
			In water	In ethyl alcohol	
acetic acid	16.6	118.1	infinite	infinite	1.05
benzene	5.5	80.1	0.07	infinite	0.879
bromine	−7.1	58.8	3.51	infinite	3.12
iron	1530	3000	insoluble	insoluble	7.86
methane	−182.5	−161.5	0.0022	0.033	0.000667
oxygen	−218.8	−183.0	0.0040	0.037	0.00133
sodium chloride	801	1473	36.5	0.065	2.16
water	0	100	—	infinite	1.00

1-5 Chemical and Physical Changes

We described the reaction of magnesium as it burns in oxygen (see Figure 1-1). This is a *chemical change* or *chemical reaction*. In any **chemical change**, (1) one or more substances are used up (at least partially), (2) one or more new substances are formed, and (3) energy is absorbed or released. As substances undergo chemical changes, they demonstrate their chemical properties. A **physical change**, on the other hand, occurs with *no change in chemical composition*. Physical properties are usually altered significantly as matter undergoes physical changes (see Figure 1-8). In addition, a physical change *may* suggest that a chemical change has also taken place. For instance, a color change, a warming, or the formation of a solid when two solutions are mixed could indicate a chemical change.

Energy is always released or absorbed when chemical or physical changes occur. Energy is absorbed when ice melts, and energy is absorbed when water boils. Conversely, the condensation of steam to form liquid water always releases energy, as does the freezing of liquid water to form ice. The changes in energy that accompany these physical changes for

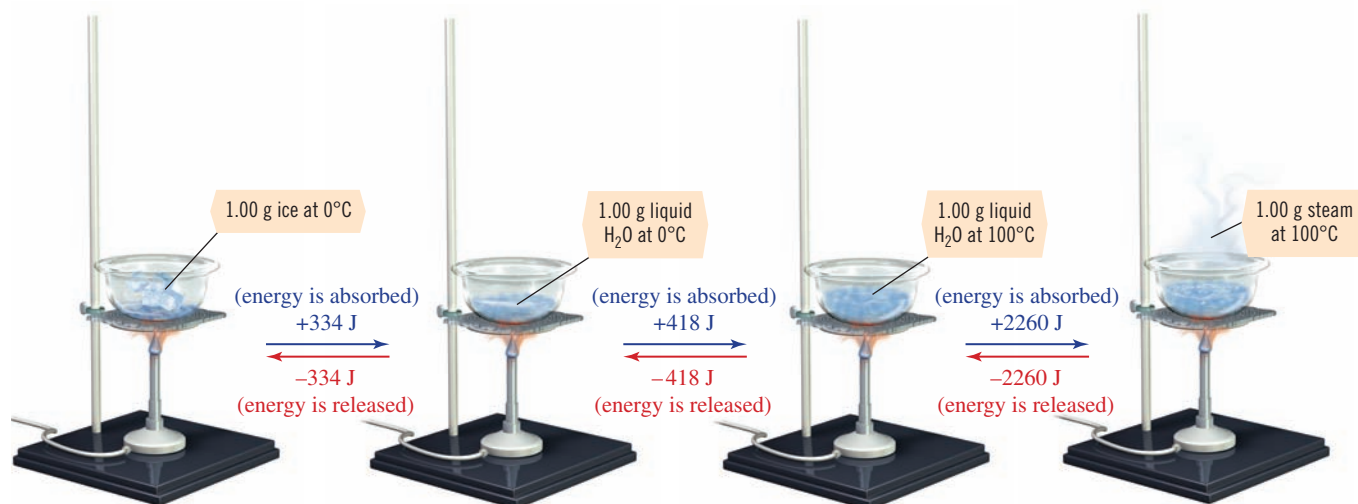


Figure 1-10 Changes in energy that accompany some physical changes for water. The energy unit joules (J) is defined in Section 1-13. Absorption of energy is denoted with a positive sign. Release of energy is denoted with a negative sign.

water are shown in Figure 1-10. At a pressure of one atmosphere, ice always melts at the same temperature (0°C), and pure water always boils at the same temperature (100°C).

1-6 Mixtures, Substances, Compounds, and Elements

A **mixture** is a combination of two or more pure substances in which each substance retains its own composition and properties. Almost every sample of matter that we ordinarily encounter is a mixture. The most easily recognized type of mixture is one that is not uniform throughout. Such a mixture, in which different portions of the sample have recognizably different properties, is called **heterogeneous**. Examples include mixtures of salt and charcoal (in which two components with different colors can be distinguished readily from each other by sight), foggy air (which includes a suspended mist of water droplets), and vegetable soup. Another kind of mixture has uniform properties throughout; such a mixture is described as a **homogeneous mixture** and is also called a **solution**. Examples include salt water; some *alloys*, which are homogeneous mixtures of metals in the solid state; and air (free of particulate matter or mists). Air is a mixture of nitrogen, oxygen, argon, carbon dioxide, and water vapor. There are only trace amounts of other substances in the atmosphere.

An important characteristic of all mixtures is that they can have variable composition. (For instance, we can make an infinite number of different mixtures of salt and sugar by varying the relative amounts of the two components used.) Consequently, repeating the same experiment on mixtures from different sources may give different results, whereas the same treatment of a pure sample will always give the same results. When the distinction between homogeneous mixtures and pure substances was realized and methods were developed (in the late 1700s) for separating mixtures and studying pure substances, consistent results were obtained. This resulted in reproducible chemical properties, which formed the basis of real progress in the development of chemistry.

A mixture can be separated by physical means because each component retains its properties (Figures 1-11 and 1-12). For example, a mixture of salt and water can be separated by evaporating the water and leaving the solid salt behind. To separate a mixture of sand and salt, we could treat it with water to dissolve the salt, collect the sand by filtration, and then evaporate the water to reclaim the solid salt. Very fine iron powder can be mixed with powdered sulfur to give what appears to the naked eye to be a homogeneous mixture of the two. Separation of the components of this mixture is easy, however. The iron may be removed by a magnet (see Figure 1-11), or the sulfur may be dissolved in carbon disulfide, which does not dissolve iron.

► By “composition of a mixture,” we mean both the identities of the substances present and their relative amounts in the mixture.

► The blue copper(II) sulfate solution in Figure 1-9c is a homogeneous mixture.



A T-bone steak is a heterogeneous mixture of white fat, bone, and red meat. Each of these macroscopic items is in turn heterogeneous. For example, the meat is composed of blood vessels, protein structures, fine tendons, etc.

Unless otherwise noted, all content on this page is © Cengage Learning.

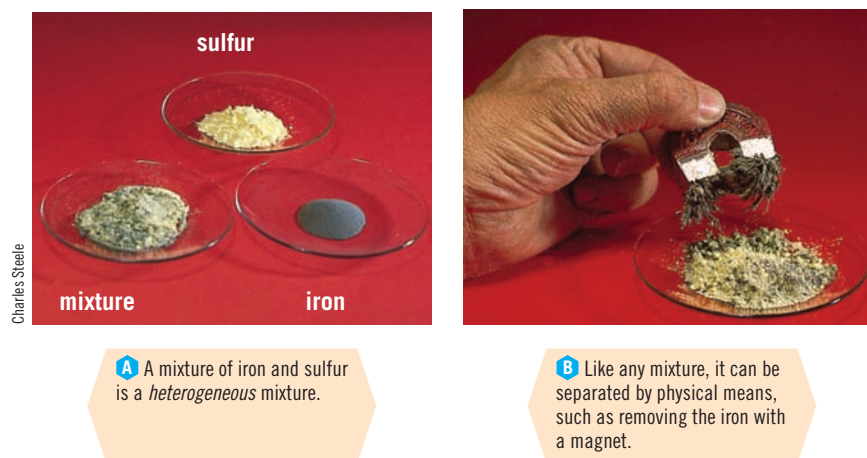


Figure 1-11 Separation by physical means.

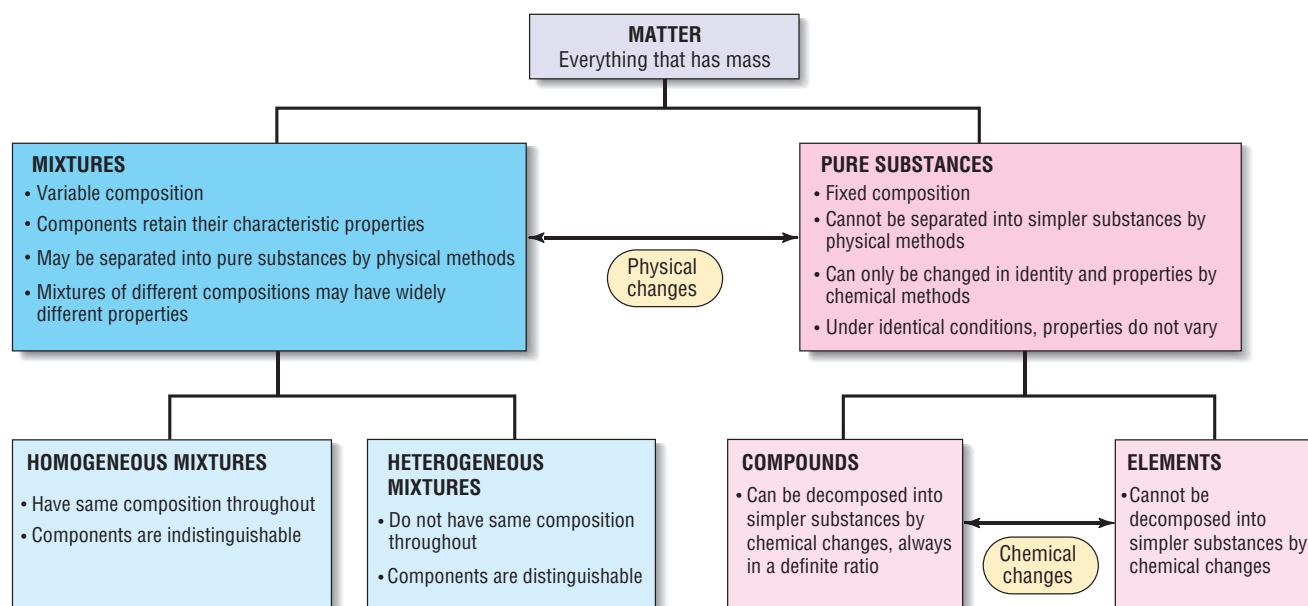


Figure 1-12 One scheme for classification of matter. Arrows indicate the general means by which matter can be separated.

In *any* mixture, (1) the composition can be varied and (2) each component of the mixture retains its own properties.

► The first ice that forms is quite pure. The dissolved solids tend to stay behind in the remaining liquid.

Suppose we have a sample of muddy river water (a heterogeneous mixture). We might first separate the suspended dirt from the liquid by filtration. Then we could remove dissolved air by warming the water. Dissolved solids might be removed by cooling the sample until some of it freezes, pouring off the liquid, and then melting the ice. Other dissolved components might be separated by distillation or other methods. Eventually we would obtain a sample of pure water that could not be further separated by any physical separation methods. No matter what the original source of the impure water—the ocean, the Mississippi River, a can of tomato juice—water samples obtained by purification all have identical composition, and, under identical conditions, they all have identical properties. Any such sample is called a *substance*, or sometimes a *pure substance*.

► If we use the definition given here of a *substance*, the phrase *pure substance* may appear to be redundant.

A **substance** cannot be further broken down or purified by physical means. A substance is matter of a particular kind. Each substance has its own characteristic properties that are different from the set of properties of any other substance.

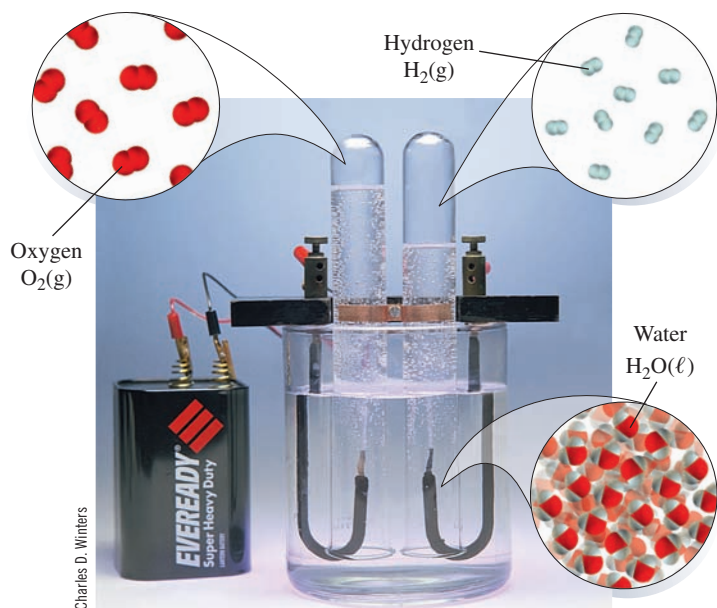


Figure 1-13 Electrolysis apparatus for small-scale chemical decomposition of liquid water by electrical energy. The volume of hydrogen gas produced (*right*) is twice that of oxygen gas (*left*). Some dilute sulfuric acid is added to increase the conductivity.

Now suppose we decompose some water by passing electricity through it (Figure 1-13). (This *electrolysis* process is a chemical reaction.) We find that the water is converted into two simpler substances, hydrogen and oxygen; furthermore, hydrogen and oxygen are *always* present in the same ratio by mass, 11.1% to 88.9%. These observations allow us to identify water as a compound.

A **compound** is a substance that can be decomposed by chemical means into simpler substances, always in the same ratio by mass.

As we continue such a process starting with any substance, we eventually reach a stage at which the new substances formed cannot be further broken down by chemical means. The substances at the end of this chain are called *elements*.

An **element** is a substance that cannot be decomposed into simpler substances by chemical changes.

For instance, neither of the two gases obtained by the electrolysis of water—hydrogen and oxygen—can be further decomposed, so we know that they are elements.

As another illustration (Figure 1-14), pure calcium carbonate (a white solid present in limestone and seashells) can be broken down by heating to give another white solid (call it A) and a gas (call it B) in the mass ratio 56.0:44.0. This observation tells us that calcium carbonate is a compound. The white solid A obtained from calcium carbonate can be further broken down into a solid and a gas in a definite ratio by mass, 71.5:28.5. But neither of these can be further decomposed, so they must be elements. The gas is identical to the oxygen obtained from the electrolysis of water; the solid is a metallic element called calcium. Similarly, the gas B, originally obtained from calcium carbonate, can be decomposed into two elements, carbon and oxygen, in a fixed mass ratio, 27.3:72.7. This sequence illustrates that a compound can be broken apart into simpler substances with a fixed mass ratio; these may be either elements or simpler compounds.

Furthermore, we may say that *a compound is a pure substance consisting of two or more different elements in a fixed ratio*. Water is 11.1% hydrogen and 88.9% oxygen by mass.

Unless otherwise noted, all content on this page is © Cengage Learning.

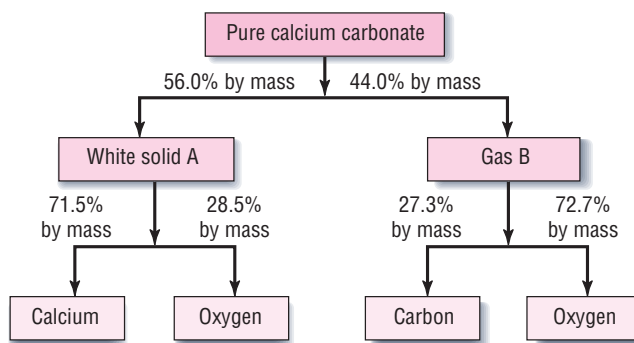


Figure 1-14 Diagram of the decomposition of calcium carbonate to give a white solid A (56.0% by mass) and a gas B (44.0% by mass). This decomposition into simpler substances at a fixed ratio proves that calcium carbonate is a compound. The white solid A further decomposes to give the elements calcium (71.5% by mass) and oxygen (28.5% by mass). This proves that the white solid A is a compound; it is known as calcium oxide. The gas B also can be broken down to give the elements carbon (27.3% by mass) and oxygen (72.7% by mass). This establishes that gas B is a compound; it is known as carbon dioxide.



Charles D. Winters

Figure 1-15 The reaction of sodium, a solid element, and chlorine, a gaseous element, to produce sodium chloride (table salt). This reaction gives off considerable energy in the form of heat and light.

Similarly, carbon dioxide is 27.3% carbon and 72.7% oxygen by mass, and calcium oxide (the white solid A in the previous discussion) is 71.5% calcium and 28.5% oxygen by mass. We could also combine the numbers in the previous paragraph to show that calcium carbonate is 40.1% calcium, 12.0% carbon, and 47.9% oxygen by mass. Observations such as these on many pure compounds led to the statement of the **Law of Definite Proportions** (also known as the **Law of Constant Composition**):

Different samples of any pure compound contain the same elements in the same proportions by mass.

The physical and chemical properties of a compound are different from the properties of its constituent elements. Sodium chloride is a white solid that we ordinarily use as table salt (Figure 1-15). This compound is formed by the combination of the element sodium (a soft, silvery white metal that reacts violently with water; see Figure 1-9d) and the element chlorine (a pale green, corrosive, poisonous gas; see the right panel of Figure 1-7).

Recall that elements are substances that cannot be decomposed into simpler substances by chemical changes. Nitrogen, silver, aluminum, copper, gold, and sulfur are other examples of elements.

We use a set of **symbols** to represent the elements. These symbols can be written more quickly than names, and they occupy less space. The symbols for the first 109 elements consist of either a capital letter *or* a capital letter and a lowercase letter, such as C (carbon) or Ca (calcium). A list of the known elements and their symbols is given inside the front cover.

In the past, the discoverers of elements claimed the right to name them, although the question of who had actually discovered the elements first was sometimes disputed. In modern times, each new element is given a temporary name and a three-letter symbol based on a numerical system. This designation is used until the question of the right to name the newly discovered element is resolved. Decisions resolving the names of elements 104 through 112 have been announced by the International Union of Pure and Applied Chemistry (IUPAC), an international organization that represents chemical societies from 40 countries. IUPAC makes recommendations regarding many matters of convention and terminology in chemistry. These recommendations carry no legal force, but they are normally viewed as authoritative throughout the world.

A short list of symbols of common elements is given in Table 1-3. Many symbols consist of the first one or two letters of the element's English name. Some are derived from the element's Latin name (indicated in parentheses in Table 1-3) and one, W for tungsten, is from the German *Wolfram*. You should learn the list in Table 1-3. Names and symbols for additional elements should be learned as they are needed.

► See the essay "Names of the Elements" on page 18.

Most of the earth's crust is made up of a relatively small number of elements. Only 10 of the 88 naturally occurring elements make up more than 99% by mass of the earth's crust, oceans, and atmosphere (Table 1-4). Oxygen accounts for roughly half, mainly in the form of water or oxide minerals. Relatively few elements, approximately one-fourth of the naturally occurring ones, occur in nature as free elements. The rest are always found chemically combined with other elements.

A very small amount of the matter in the earth's crust, oceans, and atmosphere is involved in living matter. The main element in living matter is carbon, but only a tiny fraction of the carbon in the environment occurs in living organisms. More than one-quarter of the total mass of the earth's crust, oceans, and atmosphere is made up of silicon, yet it has almost no biological role.

► The other known elements have been made artificially in laboratories, as described in Chapter 22.

Table 1-3 Some Common Elements and Their Symbols

Symbol	Element	Symbol	Element	Symbol	Element
Ag	silver (<i>argentum</i>)	F	fluorine	Ni	nickel
Al	aluminum	Fe	iron (<i>ferrum</i>)	O	oxygen
Au	gold (<i>aurum</i>)	H	hydrogen	P	phosphorus
B	boron	He	helium	Pb	lead (<i>plumbum</i>)
Ba	barium	Hg	mercury (<i>hydrargyrum</i>)	Pt	platinum
Bi	bismuth	I	iodine	S	sulfur
Br	bromine	K	potassium (<i>kalium</i>)	Sb	antimony (<i>stibium</i>)
C	carbon	Kr	krypton	Si	silicon
Ca	calcium	Li	lithium	Sn	tin (<i>stannum</i>)
Cd	cadmium	Mg	magnesium	Sr	strontium
Cl	chlorine	Mn	manganese	Ti	titanium
Co	cobalt	N	nitrogen	U	uranium
Cr	chromium	Na	sodium (<i>natrium</i>)	W	tungsten (<i>Wolfram</i>)
Cu	copper (<i>cuprum</i>)	Ne	neon	Zn	zinc



Charles Steele

Mercury is the only metal that is a liquid at room temperature.

Table 1-4 Abundance of Elements in the Earth's Crust, Oceans, and Atmosphere

Element	Symbol	% by Mass	Element	Symbol	% by Mass
oxygen	O	49.5%	chlorine	Cl	0.19%
silicon	Si	25.7	phosphorus	P	0.12
aluminum	Al	7.5	manganese	Mn	0.09
iron	Fe	4.7	carbon	C	0.08
calcium	Ca	3.4	sulfur	S	0.06
sodium	Na	2.6	barium	Ba	0.04
potassium	K	2.4	chromium	Cr	0.033
magnesium	Mg	1.9	nitrogen	N	0.030
hydrogen	H	0.87	fluorine	F	0.027
titanium	Ti	0.58	zirconium	Zr	0.023
			all others combined		≈ 0.1%



Charles Steele

The stable form of sulfur at room temperature is a solid.

Names of the Elements

If you were to discover a new element, how would you name it? Throughout history, scientists have answered this question in different ways. Most have chosen to honor a person or place or to describe the new substance.

Until the Middle Ages only nine elements were known: gold, silver, tin, mercury, copper, lead, iron, sulfur, and carbon. The metals' chemical symbols are taken from descriptive Latin names: *aurum* ("yellow"), *argentum* ("shining"), *stannum* ("dripping" or "easily melted"), *hydrargyrum* ("silvery water"), *cuprum* ("Cyprus," where many copper mines were located), *plumbum* (exact meaning unknown—possibly "heavy"), and *ferrum* (also unknown). Mercury is named after the planet, one reminder that the ancients associated metals with gods and celestial bodies. In turn, both the planet, which moves rapidly across the sky, and the element, which is the only metal that is liquid at room temperature and thus flows rapidly, are named for the fleet god of messengers in Roman mythology. In English, mercury is nicknamed "quicksilver."

Prior to the reforms of Antoine Lavoisier (1743–1794), chemistry was a largely nonquantitative, unsystematic science in which experimenters had little contact with each other. In 1787, Lavoisier published his *Methode de Nomenclature Chimique*, which proposed, among other changes, that all new elements be named descriptively. For the next 125 years, most elements were given names that corresponded to their properties. Greek roots were one popular source, as evidenced by hydrogen (*hydros-gen*, "water-producing"), oxygen (*oksys-gen*, "acid-producing"), nitrogen (*nitron-gen*, "soda-producing"), bromine (*bromos*, "stink"), and argon (*a-er-gon*, "no reaction"). The discoverers of argon, Sir William Ramsay (1852–1916) and Baron Rayleigh (1842–1919), originally proposed the name *aeron* (from *aer* or "air"), but critics thought it was too close to the biblical name Aaron! Latin roots, such as *radius* ("ray"), were also used (radium and radon are both naturally radioactive elements that emit "rays"). Color was often the determining property, especially after the invention of the spectroscope in 1859, because different elements (or the light that they emit) have prominent characteristic colors. Cesium, indium, iodine, rubidium, and thallium were all named in this manner. Their respective Greek and Latin roots denote blue-gray, indigo, violet, red, and green (*thallus* means "tree sprout"). Because of the great variety of colors of its compounds, iridium takes its name from the Latin *iris*, meaning "rainbow." Alternatively, an element name might suggest a mineral or the ore that contained it. One example is Wolfram or tungsten (W), which was isolated from wolframite. Two other "inconsistent" elemental symbols, K and Na, arose from occurrence as well. *Kalium* was first obtained from the saltwort plant, *Salsola kali*, and *natrium* from niter. Their English names, potassium and sodium, are derived from the ores potash and soda.

Other elements, contrary to Lavoisier's suggestion, were named after planets, mythological figures, places, or superstitions. "Celestial elements" include helium ("sun"), tellurium ("earth"), selenium ("moon"—the element was discovered in close proximity to tellurium), cerium (the asteroid Ceres, which was discovered only two years before the element), and uranium (the planet Uranus, discovered a few years earlier). The first two transuranium elements (those *beyond* uranium) to be produced were named neptunium and plutonium for the next two planets, Neptune and Pluto. The names promethium (Prometheus, who stole fire from heaven), vanadium (Scandinavian goddess Vanadis), titanium (Titans, the first sons of the earth), tantalum (Tantalos, father of the Greek goddess Niobe), and thorium (Thor, Scandinavian god of war) all arise from Greek or Norse mythology.

"Geographical elements," shown on the map, sometimes honored the discoverer's native country or workplace. The Latin names for Russia (*ruthenium*), France (*gallium*), Paris (*lutetium*), and Germany (*germanium*) were among those used. Marie Skłodowska Curie named one of the elements that she discovered, polonium, after her native Poland. Often the locale of discovery lends its name to the element; the record holder is certainly the Swedish village Ytterby, the site of ores from which the four elements terbium, erbium, ytterbium, and yttrium were isolated. Elements honoring important scientists include curium, einsteinium, nobelium, fermium, and lawrencium.

Most of the elements now known were given titles peacefully, but a few were not. Niobium, isolated in 1803 by Ekeberg from an ore that also contained tantalum, and named after Niobe (daughter of Tantalos), was later found to be identical to an 1802 discovery of C. Hatchett, columbium. (Interestingly, Hatchett first found the element in an ore sample that had been sent to England more than a century earlier by John Winthrop, the first governor of Connecticut.) Although "niobium" became the accepted designation in Europe, the Americans, not surprisingly, chose "columbium." It was not until 1949—when the International Union of Pure and Applied Chemistry (IUPAC) ended more than a century of controversy by ruling in favor of mythology—that element 41 received a unique name.

In 1978, the IUPAC recommended that elements beyond 103 be known temporarily by systematic names based on numerical roots; element 104 is unnilquadium (*un* for 1, *nil* for 0, *quad* for 4, plus the *-ium* ending), followed by unnilpentium, unnilhexium, and so on. Arguments over the names of elements 104 and 105 prompted the IUPAC to begin hearing claims of priority to numbers 104 to 109. The IUPAC's final recommendations for these element names were announced in 1997. The names and symbols recommended by that report are: element 104, rutherfordium, Rf; element 105, dubnium, Db; element 106, seaborgium, Sg; element 107, bohrium, Bh; element 108, hassium, Hs; and element 109, meitnerium, Mt. Some of these (Rf and Bh) are derived from the names of scientists prominent in the development of atomic theory; others (Sg, Hs, and Mt) are named for scientists who were involved in the discovery of heavy elements. Dubnium is named in honor of the Dubna laboratory in the former Soviet Union, where important contributions to the creation of heavy elements have originated.

LISA SAUNDERS BAUGH



Many chemical elements were named after places. From Vivi Ringnes, "Origin and Names of Chemical Elements," *Journal of Chemical Education*, 66, 1989, 731–737. Reprinted by permission.

1-7 Measurements in Chemistry

In the next section, we will introduce the standards for basic units of measurement. These standards were selected because they are reproducible and unchanging and because they allow us to make precise measurements. The values of fundamental units are arbitrary.¹ In the United States, all units of measure are set by the National Institute of Standards and Technology, NIST (formerly the National Bureau of Standards, NBS). Measurements in the scientific world are usually expressed in the units of the metric system or its modernized successor, the International System of Units (SI). The SI, adopted by the National Bureau of Standards in 1964, is based on the seven fundamental units listed in Table 1-5. All other units of measurement are derived from them.

► The abbreviation SI comes from the French *le Système International*.

In this text we shall use both metric units and SI units. Conversions between non-SI and SI units are usually straightforward. Appendix C lists some important units of measurement and their relationships to one another. Appendix D lists several useful physical constants. The most frequently used of these appear on the inside back cover.

The metric and SI systems are *decimal systems, in which prefixes are used to indicate fractions and multiples of ten*. The same prefixes are used with all units of measurement. The distances and masses in Table 1-6 illustrate the use of some common prefixes and the relationships among them.

Table 1-5 The Seven Fundamental Units of Measurement (SI)

Physical Property	Name of Unit	Symbol
length	meter	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
temperature	kelvin	K
luminous intensity	candela	cd
amount of substance	mole	mol

Table 1-6 Common Prefixes Used in the SI and Metric Systems

Prefix	Abbreviation	Meaning	Example
mega-	M	10^6	1 megameter (Mm) = 1×10^6 m
kilo-*	k	10^3	1 kilometer (km) = 1×10^3 m
deci-	d	10^{-1}	1 decimeter (dm) = 1×10^{-1} m
centi-*	c	10^{-2}	1 centimeter (cm) = 1×10^{-2} m
milli-*	m	10^{-3}	1 milligram (mg) = 1×10^{-3} g
micro-*	$\mu^\dagger$	10^{-6}	1 microgram (μg) = 1×10^{-6} g
nano-*	n	10^{-9}	1 nanogram (ng) = 1×10^{-9} g
pico-*	p	10^{-12}	1 picogram (pg) = 1×10^{-12} g

► The prefixes used in the SI and metric systems may be thought of as *multipliers*. For example, the prefix *kilo-* indicates multiplication by 1000 or 10^3 , and *milli-* indicates multiplication by 0.001 or 10^{-3} .

*These prefixes are commonly used in chemistry.

[†]This is the Greek letter μ (pronounced “mew”).

¹Prior to the establishment of the National Bureau of Standards in 1901, at least 50 different distances had been used as “1 foot” in measuring land within New York City. Thus the size of a 100-ft by 200-ft lot in New York City depended on the generosity of the seller and did not necessarily represent the expected dimensions.

1-8 Units of Measurement

Mass and Weight

We distinguish between mass and weight. **Mass** is the measure of the quantity of matter a body contains (see Section 1-1). The mass of a body does not vary as its position changes. On the other hand, the **weight** of a body is a measure of the gravitational attraction of the earth for the body, and this varies with distance from the center of the earth. An object weighs very slightly less high up on a mountain than at the bottom of a deep valley. Because the mass of a body does not vary with its position, the mass of a body is a more fundamental property than its weight. We have become accustomed, however, to using the term “weight” when we mean mass, because weighing is one way of measuring mass (Figure 1-16). Because we usually discuss chemical reactions at constant gravity, weight relationships are just as valid as mass relationships. Nevertheless, we should keep in mind that the two are not identical.

The basic unit of mass in the SI system is the **kilogram** (Table 1-7). The kilogram is defined as the mass of a platinum–iridium cylinder stored in a vault in Sèvres, near Paris, France. A 1-lb object has a mass of 0.4536 kg. The basic mass unit in the earlier *metric system* was the gram. A U.S. five-cent coin (a “nickel”) has a mass of about 5 g.

Length

The **meter** is the standard unit of length (distance) in both SI and metric systems. The meter is defined as the distance light travels in a vacuum in $1/299,792,468$ second. It is approximately 39.37 inches. In situations in which the English system would use inches, the

Table 1-7 Some SI Units of Mass

kilogram, kg	base unit
gram, g	$1,000 \text{ g} = 1 \text{ kg}$
milligram, mg	$1,000 \text{ mg} = 1 \text{ g}$
microgram, μg	$1,000,000 \mu\text{g} = 1 \text{ g}$



A A triple-beam balance used for determining mass to about $\pm 0.01 \text{ g}$



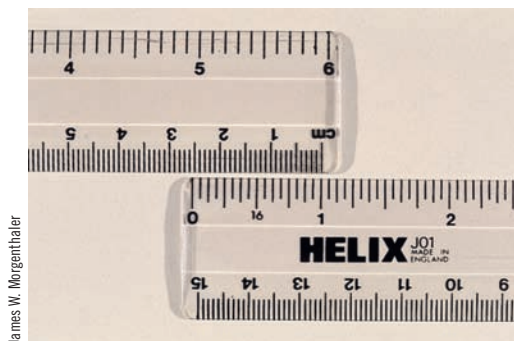
B A modern electronic top-loading balance that gives a direct readout of mass to $\pm 0.001 \text{ g}$



C A modern analytical balance that can be used to determine mass to $\pm 0.0001 \text{ g}$. Analytical balances are used when masses must be determined as precisely as possible.

Figure 1-16 Three types of laboratory balances.

Unless otherwise noted, all content on this page is © Cengage Learning.



James W. Morgenthaler

Figure 1-17 The relationship between inches and centimeters: 1 in. = 2.54 cm (exactly).

metric centimeter (1/100 meter) is convenient. The relationship between inches and centimeters is shown in Figure 1-17.

Volume

Volumes are often measured in liters or milliliters in the metric system. One liter (1 L) is one cubic decimeter (1 dm³), or 1000 cubic centimeters (1000 cm³). One milliliter (1 mL) is 1 cm³. In medical laboratories, the cubic centimeter (cm³) is often abbreviated cc. In the SI, the cubic meter is the basic volume unit and the cubic decimeter replaces the metric unit, liter. Different kinds of glassware are used to measure the volume of liquids. The one we choose depends on the accuracy we desire. For example, the volume of a liquid dispensed can be measured more accurately with a buret than with a small graduated cylinder (Figure 1-18). Some equivalences between common English units and metric units are summarized in Table 1-8.

Sometimes we must combine two or more units to describe a quantity. For instance, we might express the speed of a car as 60 mi/h (also mph). Recall that the algebraic notation x^{-1} means $1/x$; applying this notation to units, we see that h⁻¹ means 1/h, or “per hour.” So the unit of speed could also be expressed as mi · h⁻¹.



Charles D. Winters

Figure 1-18 Some laboratory apparatus used to measure volumes of liquids: 150-mL beaker (*bottom left*, green liquid); 25-mL buret (*top left*, red); 1000-mL volumetric flask (*center*, yellow); 100-mL graduated cylinder (*right front*, blue); and 10-mL volumetric pipet (*right rear*, green).

► The meter was originally defined (1791) as one ten-millionth of the distance between the North Pole and the equator.

Table 1-8 Some Conversion Factors Relating Length, Volume, and Mass (Weight) Units

	Metric		English		Metric-English Equivalents	
Length	1 km	= 10 ³ m	1 ft	= 12 in.	2.54 cm	= 1 in.
	1 cm	= 10 ⁻² m	1 yd	= 3 ft	39.37 in.*	= 1 m
	1 mm	= 10 ⁻³ m	1 mi	= 5280 ft	1.609 km*	= 1 mi
	1 nm	= 10 ⁻⁹ m				
	1 Å	= 10 ⁻¹⁰ m				
Volume	1 mL	= 1 cm ³ = 10 ⁻³ L	1 gal	= 4 qt = 8 pt	1 L	= 1.057 qt*
	1 m ³	= 10 ⁶ cm ³ = 10 ³ L	1 qt	= 57.75 in. ³ *	28.32 L	= 1 ft ³ *
Mass	1 kg	= 10 ³ g	1 lb	= 16 oz	453.6 g*	= 1 lb
	1 mg	= 10 ⁻³ g			1 g	= 0.03527 oz*
	1 metric tonne	= 10 ³ kg	1 short ton	= 2000 lb	1 metric tonne	= 1.102 short ton*

*These conversion factors, unlike the others listed, are inexact. They are quoted to four significant figures, which is ordinarily sufficient.

Unless otherwise noted, all content on this page is © Cengage Learning.

1-9 The Unit Factor Method (Dimensional Analysis)

Many chemical and physical processes can be described by numerical relationships. In fact, many of the most useful ideas in science must be treated mathematically. In chemistry, we measure and calculate many things, so we must understand how to use numbers. Two aspects of numbers are: (1) the notation of very large and very small numbers (scientific notation) and (2) an indication of how well we actually know the numbers we are using (significant figures). You will carry out many calculations with calculators. Please refer to Appendix A for a review of scientific notation and significant figures, and for some instructions about the use of electronic calculators. In this section, we review some problem-solving skills.

► It would be meaningless to say that the length of a piece of cloth is 4.7. We must specify units with the number—4.7 inches, 4.7 feet, or 4.7 meters, for instance.

Units must *always* accompany the numeric value of a measurement, whether we are writing about the quantity, talking about it, or using it in calculations.

Multiplication by unity (by one) does not change the value of an expression. If we represent “one” in a useful way, we can do many conversions by just “multiplying by one.” This method of performing calculations is known as **dimensional analysis**, the **factor-label method**, or the **unit factor method**. Regardless of the name chosen, it is a powerful mathematical tool that is almost foolproof.

Unit factors may be constructed from any two terms that describe the same or equivalent “amounts” of whatever we may consider. For example, 1 foot is equal to exactly 12 inches, by definition. We may write an equation to describe this equality:

$$1 \text{ ft} = 12 \text{ in.}$$

Dividing both sides of the equation by 1 ft gives

$$\frac{1 \text{ ft}}{1 \text{ ft}} = \frac{12 \text{ in.}}{1 \text{ ft}} \quad \text{or} \quad 1 = \frac{12 \text{ in.}}{1 \text{ ft}}$$

The factor (fraction) 12 in./1 ft is a unit factor because the numerator and denominator describe the same distance. Dividing both sides of the original equation by 12 in. gives $1 = 1 \text{ ft}/12 \text{ in.}$, a second unit factor that is the reciprocal of the first. *The reciprocal of any unit factor is also a unit factor.* Stated differently, division of an amount by the same amount always yields one!

In the English system, we can write many unit factors, such as

$$\frac{1 \text{ yd}}{3 \text{ ft}}, \frac{1 \text{ yd}}{36 \text{ in.}}, \frac{1 \text{ mi}}{5280 \text{ ft}}, \frac{4 \text{ qt}}{1 \text{ gal}}, \frac{2000 \text{ lb}}{1 \text{ ton}}$$

The reciprocal of each of these is also a unit factor. Items in retail stores are frequently priced with unit factors, such as 39¢/lb and \$3.98/gal. When all the quantities in a unit factor come from definitions, the unit is known to an unlimited (infinite) number of significant figures. For instance, if you bought eight 1-gallon jugs of something priced at \$3.98/gal, the total cost would be $8 \times \$3.98$, or \$31.84; the merchant would not round this to \$31.80, let alone to \$30.

In science, nearly all numbers have units. What does 12 mean? Usually we must supply appropriate units, such as 12 eggs or 12 people. In the unit factor method, the units guide us through calculations in a step-by-step process, because all units except those in the desired result cancel.

EXAMPLE 1-3 Unit Factors

Express 1.47 miles in inches.

Plan

First we write down the units of what we wish to know, preceded by a question mark. Then we set it equal to whatever we are given:

$$\underline{\hspace{1cm}} \text{ inches} = 1.47 \text{ miles}$$

Then we choose unit factors to convert the given units (miles) to the desired units (inches):

$$\text{miles} \longrightarrow \text{feet} \longrightarrow \text{inches}$$

Solution

$$\underline{\hspace{1cm}} \text{ in.} = 1.47 \text{ mi} \times \frac{5280 \text{ ft}}{1 \text{ mi}} \times \frac{12 \text{ in.}}{1 \text{ ft}} = 9.31 \times 10^4 \text{ in.} \text{ (calculator gives 93139.2)}$$

Note that both miles and feet cancel, leaving only inches, the desired unit. Thus, there is no ambiguity as to how the unit factors should be written. The answer contains three significant figures because there are three significant figures in 1.47 miles.

► We relate (a) miles to feet and then (b) feet to inches.

STOP & THINK

The conversion factors give correct units (inches). An inch is much shorter than a mile, so it makes sense that the number of inches is much larger than the number of miles. Cancellation of units will be omitted in the remainder of this book, but you may find it useful to continue cancelling units.

Problem-Solving Tip Significant Figures

“How do defined quantities affect significant figures?” Any quantity that comes from a *definition* is exact, that is, it is known to an unlimited number of significant figures. In Example 1-3, the quantities 5280 ft, 1 mile, 12 in., and 1 ft all come from definitions, so they do not limit the significant figures in the answer.

Problem-Solving Tip Think About Your Answer!

It is often helpful to ask yourself, “Does the answer make sense?” In Example 1-3, the distance involved is more than a mile. We expect this distance to be many inches, so a large answer is not surprising. Suppose we had mistakenly multiplied by the unit factor $\frac{1 \text{ mile}}{5280 \text{ feet}}$ (and not noticed that the units did not cancel properly); we would have gotten the answer $3.34 \times 10^{-3} \text{ in.}$ (0.00334 in.), which we should have immediately recognized as nonsense!

Within the SI and metric systems, many measurements are related to one another by powers of ten.

EXAMPLE 1-4 Unit Conversions

The Ångstrom (Å) is a unit of length, $1 \times 10^{-10} \text{ m}$, that provides a convenient scale on which to express the radii of atoms. Radii of atoms are often expressed in picometers. The radius of a phosphorus atom is 1.10 Å . What is the distance expressed in centimeters and picometers?

Plan

We use the equalities $1 \text{ Å} = 1 \times 10^{-10} \text{ m}$, $1 \text{ cm} = 1 \times 10^{-2} \text{ m}$, and $1 \text{ pm} = 1 \times 10^{-12} \text{ m}$ to construct the unit factors that convert 1.10 Å to the desired units.

Solution

$$\underline{\hspace{1cm}} \text{ cm} = 1.10 \text{ Å} \times \frac{1 \times 10^{-10} \text{ m}}{1 \text{ Å}} \times \frac{1 \text{ cm}}{1 \times 10^{-2} \text{ m}} = 1.10 \times 10^{-8} \text{ cm}$$

$$\underline{\hspace{1cm}} \text{ pm} = 1.10 \text{ Å} \times \frac{1.0 \times 10^{-10} \text{ m}}{1 \text{ Å}} \times \frac{1 \text{ pm}}{1 \times 10^{-12} \text{ m}} = 1.10 \times 10^2 \text{ pm}$$

You should now work Exercise 36.

$$\begin{array}{l} \text{Å} \rightarrow \text{m} \rightarrow \text{cm} \\ \text{Å} \rightarrow \text{m} \rightarrow \text{pm} \end{array}$$

STOP & THINK

All the unit factors in Example 1-4 are exact numbers. One cm is longer than one Å, so the number of cm is less than the number of Å. One pm is shorter than one Å, so the number of pm is greater than the number of Å.

EXAMPLE 1-5 Volume Calculation

Assuming a phosphorus atom is spherical, calculate its volume in $\text{\AA}^3$, cm^3 , and nm^3 . The formula for the volume of a sphere is $V = \left(\frac{4}{3}\right)\pi r^3$. Refer to Example 1-4.

Plan

We use the results of Example 1-4 to calculate the volume in each of the desired units.

Solution

$$\underline{} \text{ \AA}^3 = \left(\frac{4}{3}\right)\pi(1.10 \text{ \AA})^3 = 5.38 \text{ \AA}^3$$

$$\underline{} \text{ cm}^3 = \left(\frac{4}{3}\right)\pi(1.10 \times 10^{-8} \text{ cm})^3 = 5.58 \times 10^{-24} \text{ cm}^3$$

$$\underline{} \text{ nm}^3 = \left(\frac{4}{3}\right)\pi(1.10 \times 10^{-1} \text{ nm})^3 = 5.58 \times 10^{-3} \text{ nm}^3$$

You should now work Exercise 38.

STOP & THINK

$$1 \text{ \AA} = 10^{-10} \text{ m} = 10^{-8} \text{ cm}$$

Be sure to cube each unit of distance as well as its magnitude.

STOP & THINK

All the unit factors in this example are exact numbers. The units of the answers are correct. One gram is a larger mass than one milligram, so the mass expressed in g should be less than that in mg. One kilogram is even larger, so the mass expressed in kg should be even smaller.

EXAMPLE 1-6 Mass Conversion

A sample of gold has a mass of 0.234 mg. What is its mass in g? in kg?

Plan

We use the relationships $1 \text{ g} = 1000 \text{ mg}$ and $1 \text{ kg} = 1000 \text{ g}$ to write the required unit factors.

Solution

$$\underline{} \text{ g} = 0.234 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}} = 2.34 \times 10^{-4} \text{ g}$$

$$\underline{} \text{ kg} = 2.34 \times 10^{-4} \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 2.34 \times 10^{-7} \text{ kg}$$

This example includes unit factors that contain only exact numbers.

Problem-Solving Tip Conversions Within the Metric or SI System

The SI and metric systems of units are based on powers of ten. This means that many unit conversions *within* these systems can be carried out just by shifting the decimal point. For instance, the conversion from milligrams to grams in Example 1-6 just involves shifting the decimal point to the *left* by three places. How do we know to move it to the left? We know that the gram is a larger unit of mass than the milligram, so the number of grams in a given mass must be a *smaller* number than the number of milligrams. After you carry out many such conversions using unit factors, you will probably begin to take such shortcuts. Always think about the answer, to see whether it should be larger or smaller than the quantity was before conversion.

Unity raised to *any* power is 1. *Any* unit factor raised to a power is still a unit factor, as the next example shows.

EXAMPLE 1-7 Volume Conversion

One liter is exactly 1000 cm^3 . How many cubic inches are there in 1000 cm^3 ?

Plan

We would multiply by the unit factor $\frac{1 \text{ in.}}{2.54 \text{ cm}}$ to convert cm to in. Here we require the *cube* of this unit factor.

Solution

$$\underline{} \text{ in.}^3 = 1000 \text{ cm}^3 \times \left(\frac{1 \text{ in.}}{2.54 \text{ cm}} \right)^3 = 1000 \text{ cm}^3 \times \frac{1 \text{ in.}^3}{16.4 \text{ cm}^3} = 61.0 \text{ in}^3$$

Example 1-7 shows that a unit factor *cubed* is still a unit factor.

EXAMPLE 1-8 Energy Conversion

A common unit of energy is the erg. Convert $3.74 \times 10^{-2} \text{ erg}$ to the SI units of energy, joules and kilojoules. One erg is exactly $1 \times 10^{-7} \text{ joule (J)}$.

Plan

The definition that relates ergs and joules is used to generate the needed unit factor. The second conversion uses a unit factor that is based on the definition of the prefix *kilo-*.

Solution

$$\underline{} \text{ J} = 3.74 \times 10^{-2} \text{ erg} \times \frac{1 \times 10^{-7} \text{ J}}{1 \text{ erg}} = 3.74 \times 10^{-9} \text{ J}$$

$$\underline{} \text{ kJ} = 3.74 \times 10^{-9} \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 3.74 \times 10^{-12} \text{ kJ}$$

Conversions between the English and SI (metric) systems are conveniently made by the unit factor method. Several conversion factors are listed in Table 1-8. It may be helpful to remember one each for

length	1 in. = 2.54 cm (exact)
mass and weight	1 lb = 454 g (near sea level)
volume	1 qt = 0.946 L or 1 L = 1.06 qt

EXAMPLE 1-9 English-Metric Conversion

Express 1.0 gallon in milliliters.

Plan

We ask $\underline{} \text{ mL} = 1.0 \text{ gal}$ and multiply by the appropriate factors.

gallons $\rightarrow$ quarts $\rightarrow$ liters $\rightarrow$ milliliters

Solution

$$\underline{} \text{ mL} = 1.0 \text{ gal} \times \frac{4 \text{ qt}}{1 \text{ gal}} \times \frac{1 \text{ L}}{1.06 \text{ qt}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 3.8 \times 10^3 \text{ mL}$$

You should now work Exercise 40.

► Suppose we start with the equality

$$1 \text{ in.} = 2.54 \text{ cm}$$

We can perform the same operation on both sides of the equation. Let's cube both sides:

$$(1 \text{ in.})^3 = (2.54 \text{ cm})^3 = 16.4 \text{ cm}^3$$

so the quantity

$$\left(\frac{1 \text{ in.}}{2.54 \text{ cm}} \right)^3$$

is a unit factor.

STOP & THINK

The erg is a smaller energy unit than the joule (or than a kilojoule, which is even larger than a joule), so the energy expressed in J or in kJ must be smaller than when it is expressed in ergs.

► We relate
(a) gallons to quarts, then
(b) quarts to liters, and then
(c) liters to milliliters.

STOP & THINK

One milliliter is a smaller volume than one liter, which is about the same as one quart; one quart is a smaller volume than one gallon. Thus it makes sense that the volume expressed in milliliters is greater than that expressed in gallons.

The fact that all other units cancel to give the desired unit, milliliters, shows that we used the correct unit factors. The factors 4 qt/gal and 1000 mL/L contain only exact numbers. The factor 1 L/1.06 qt contains three significant figures. Because 1.0 gal contains only two, the answer contains only two significant figures.

Examples 1-3 through 1-9 show that multiplication by one or more unit factors changes the units and the number of units, but not the amount of whatever we are calculating.

1-10 Percentage

We often use percentages to describe quantitatively how a total is made up of its parts. In Table 1-4, we described the amounts of elements present in terms of the percentage of each element.

Percentages can be treated as unit factors. For any mixture containing substance A,

$$\begin{array}{c} \boxed{\begin{array}{c} \% \text{ A} \\ \text{(by mass)} = \frac{\text{parts A (by mass)}}{100 \text{ parts mixture (by mass)}} \end{array}} \\ \text{mass A} \longleftrightarrow \text{mass mixture} \end{array}$$

If we say that a sample is 24.4% carbon by mass, we mean that out of every 100 parts (exactly) by mass of sample, 24.4 parts by mass are carbon. This relationship can be represented by whichever of the two unit factors we find useful:

$$\frac{24.4 \text{ parts carbon}}{100 \text{ parts sample}} \quad \text{or} \quad \frac{100 \text{ parts sample}}{24.4 \text{ parts carbon}}$$

This ratio can be expressed in terms of grams of carbon for every 100 grams of sample, pounds of carbon for every 100 pounds of sample, or any other mass or weight unit. The next example illustrates the use of dimensional analysis involving percentage.

EXAMPLE 1-10 Percentage

U.S. pennies made since 1982 consist of 97.6% zinc and 2.4% copper. The mass of a particular penny is measured to be 1.494 grams. How many grams of zinc does this penny contain?

Plan

From the percentage information given, we may write the required unit factor

$$\frac{97.6 \text{ g zinc}}{100 \text{ g sample}}$$

Solution

$$\underline{\hspace{1cm}} \text{ g zinc} = 1.494 \text{ g sample} \times \frac{97.6 \text{ g zinc}}{100 \text{ g sample}} = 1.46 \text{ g zinc}$$

The number of significant figures in the result is limited by the three significant figures in 97.6%. Because the definition of percentage involves *exactly* 100 parts, the number 100 is known to an infinite number of significant figures. The value “97.6% zinc” tells us that the penny is almost all zinc; thus the mass of zinc present is only slightly smaller than the total mass of the penny.

You should now work Exercises 67 and 68.



Charles Steele

Six materials with different densities. The liquid layers are gasoline (*top*), water (*middle*), and mercury (*bottom*). A cork floats on gasoline. A piece of oak wood sinks in gasoline but floats on water. Brass sinks in water but floats on mercury.

1-11 Density and Specific Gravity

In science, we use many terms that involve combinations of different units. Such quantities may be thought of as unit factors that can be used to convert among these units. The **density** of a sample of matter is defined as the mass per unit volume:

$$\text{density} = \frac{\text{mass}}{\text{volume}} \quad \text{or} \quad D = \frac{m}{V}$$

Table 1-9 Densities of Common Substances*

Substance	Density (g/cm ³)	Substance	Density (g/cm ³)
hydrogen (gas)	0.000089	sand*	2.32
carbon dioxide (gas)	0.0019	aluminum	2.70
cork*	0.21	iron	7.86
oak wood*	0.71	copper	8.92
ethyl alcohol	0.789	silver	10.50
water	1.00	lead	11.34
magnesium	1.74	mercury	13.59
table salt	2.16	gold	19.30

*Cork, oak wood, and sand are common materials that have been included to provide familiar reference points. They are *not* pure elements or compounds as are the other substances listed.

Densities may be used to distinguish between two substances or to assist in identifying a particular substance. They are usually expressed as g/cm³ or g/mL for liquids and solids and as g/L for gases. These units can also be expressed as g·cm⁻³, g·mL⁻¹, and g·L⁻¹, respectively. Densities of several substances are listed in Table 1-9.

EXAMPLE 1-11 Density, Mass, Volume

A 47.3-mL sample of ethyl alcohol (ethanol) has a mass of 37.32 g. What is its density?

Plan

We use the definition of density.

Solution

$$D = \frac{m}{V} = \frac{37.32 \text{ g}}{47.3 \text{ mL}} = 0.789 \text{ g/mL}$$

You should now work Exercise 44.

EXAMPLE 1-12 Density, Mass, Volume

If 116 g of ethanol is needed for a chemical reaction, what volume of liquid would you use?

Plan

We determined the density of ethanol in Example 1-11. Here we are given the mass, m , of a sample of ethanol. So we know values for D and m in the relationship

$$D = \frac{m}{V}$$

We rearrange this relationship to solve for V , put in the known values, and carry out the calculation. Alternatively, we can use the unit factor method to solve the problem.

Solution

The density of ethanol is 0.789 g/mL (see Table 1-9).

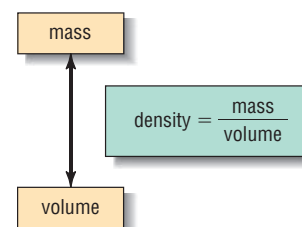
$$D = \frac{m}{V}, \text{ so } V = \frac{m}{D} = \frac{116 \text{ g}}{0.789 \text{ g/mL}} = 147 \text{ mL}$$

Alternatively,

$$\underline{\hspace{1cm}} \text{ mL} = 116 \text{ g} \times \frac{1 \text{ mL}}{0.789 \text{ g}} = 147 \text{ mL}$$

You should now work Exercise 46.

► These densities are given at room temperature and *one atmosphere* of pressure, the average atmospheric pressure at sea level. Densities of solids and liquids change only slightly, but densities of gases change greatly, with changes in temperature and pressure.



The intensive property *density* relates the two extensive properties: *mass* and *volume*.

STOP & THINK

The mass in grams is a smaller number than the volume in milliliters. Thus the density in g/mL must be less than one.

► Observe that density gives two unit factors. In this case, they are

$$\frac{0.789 \text{ g}}{1 \text{ mL}} \text{ and } \frac{1 \text{ mL}}{0.789 \text{ g}}$$

STOP & THINK

Cancellation of units leads to the correct final units (mL). A density less than one (0.789 g/mL) tells us that one mL has a mass less than one gram. Thus the number of mL needed must be numerically greater than the number of grams required.



Charles D. Winters

Ice is slightly less dense than liquid water, so ice floats in water.



Charles D. Winters

Solid ethyl alcohol is more dense than liquid ethyl alcohol. This is true of nearly every known substance.

EXAMPLE 1-13 Unit Conversion

Express the density of mercury in lb/ft³.

Plan

The density of mercury is 13.59 g/cm³ (see Table 1-9). To convert this value to the desired units, we can use unit factors constructed from the conversion factors in Table 1-8.

Solution

$$\frac{? \text{ lb}}{\text{ft}^3} = 13.59 \frac{\text{g}}{\text{cm}^3} \times \frac{1 \text{ lb}}{453.6 \text{ g}} \times \left(\frac{2.54 \text{ cm}}{1 \text{ in.}}\right)^3 \times \left(\frac{12 \text{ in.}}{1 \text{ ft}}\right)^3 = 848.4 \text{ lb/ft}^3$$

It would take a very strong person to lift a cubic foot of mercury!

STOP & THINK

Unit factors lead to the correct answer. Remember to cube the length units to convert to volume units.

► Density and specific gravity are both intensive properties; that is, they do not depend on the size of the sample. Specific gravities are dimensionless numbers.

The **specific gravity** (Sp. Gr.) of a substance is the ratio of its density to the density of water, both at the same temperature.

$$\text{Sp. Gr.} = \frac{D_{\text{substance}}}{D_{\text{water}}}$$

The density of water is 1.000 g/mL at 3.98°C, the temperature at which the density of water is greatest. Variations in the density of water with changes in temperature, however, are small enough that we can use 1.00 g/mL up to 25°C without introducing significant errors into our calculations.

EXAMPLE 1-14 Density, Specific Gravity

The density of table salt is 2.16 g/mL at 20°C. What is its specific gravity?

Plan

We use the preceding definition of specific gravity. The numerator and denominator have the same units, so the result is dimensionless.

Solution

$$\text{Sp. Gr.} = \frac{D_{\text{salt}}}{D_{\text{water}}} = \frac{2.16 \text{ g/mL}}{1.00 \text{ g/mL}} = 2.16$$

Labels on commercial solutions of acids give specific gravities and the percentage by mass of the acid present in the solution. From this information, the amount of acid present in a given volume of solution can be calculated.

STOP & THINK

Example 1-14 demonstrates that the density and specific gravity of a substance are numerically equal near room temperature if density is expressed in g/mL (or in g/cm³).

EXAMPLE 1-15 Specific Gravity, Volume, Percentage by Mass

Battery acid is 40.0% sulfuric acid, H_2SO_4 , and 60.0% water by mass. Its specific gravity is 1.31. Calculate the mass of pure H_2SO_4 in 100.0 mL of battery acid.

Plan

The percentages are given on a mass basis, so we must first convert the 100.0 mL of acid solution (soln) to mass. To do this, we need a value for the density. We have demonstrated that density and specific gravity are numerically equal at 20°C because the density of water is 1.00 g/mL. We can use the density as a unit factor to convert the given volume of the solution to mass of the solution. Then we use the percentage by mass to convert the mass of the solution to the mass of the acid.

Solution

From the given value for specific gravity, we may write

$$\text{Density} = 1.31 \text{ g/mL}$$

The solution is 40.0% H_2SO_4 and 60.0% H_2O by mass. From this information we can construct the desired unit factor:

$$\frac{40.0 \text{ g H}_2\text{SO}_4}{100 \text{ g soln}} \longrightarrow \text{because 100 g of solution contains 40.0 g of H}_2\text{SO}_4$$

We can now solve the problem:

$$\text{? H}_2\text{SO}_4 = 100.0 \text{ mL soln} \times \frac{1.31 \text{ g soln}}{1 \text{ mL soln}} \times \frac{40.0 \text{ g H}_2\text{SO}_4}{100 \text{ g soln}} = 52.4 \text{ g H}_2\text{SO}_4$$

You should now work Exercise 52.

STOP & THINK

Careful use of unit factors helps you set up the solution to Example 1-15.

1-12 Heat and Temperature

In Section 1-1 you learned that heat is one form of energy. You also learned that the many forms of energy can be interconverted and that in chemical reactions, chemical energy is converted to heat energy or vice versa. The amount of heat a process uses (*endothermic*) or gives off (*exothermic*) can tell us a great deal about that process. For this reason, it is important for us to be able to measure the intensity of heat.

Temperature measures the intensity of heat, the “hotness” or “coldness” of a body. A piece of metal at 100°C feels hot to the touch, whereas an ice cube at 0°C feels cold. Why? Because the temperature of the metal is higher, and that of the ice cube lower, than body temperature. **Heat** is a form of energy that *always flows spontaneously from a hotter body to a colder body*—it never flows in the reverse direction.

Temperatures can be measured with liquid-in-glass thermometers. This kind of thermometer consists of a reservoir of liquid at the base of a glass tube, open to a very thin (capillary) column extending upward. Any liquid expands as its temperature rises. As it expands, its movement up into the evacuated column can be seen.

Anders Celsius (1701–1744), a Swedish astronomer, developed the Celsius temperature scale, formerly called the centigrade temperature scale. When we place a Celsius thermometer in a beaker of crushed ice and water, the liquid level stands at exactly 0°C , the lower reference point. In a beaker of water boiling at one atmosphere pressure, the liquid level stands at exactly 100°C , the higher reference point. There are 100 equal steps between these two liquid levels. They correspond to an interval of 100 degrees between the melting point of ice and the boiling point of water at one atmosphere. Figure 1-19 shows how temperature marks between the reference points are established.

In the United States, temperatures are frequently measured on the temperature scale devised by Gabriel Fahrenheit (1686–1736), a German instrument maker. On this scale,

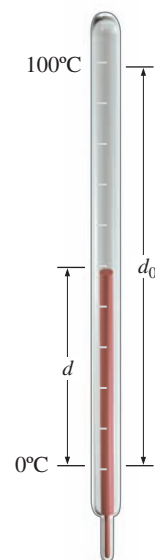


Figure 1-19 At 45°C , as read on a liquid-in-glass thermometer, d equals $0.45 d_0$, where d_0 is the distance from the liquid level at 0°C to the level at 100°C .

Unless otherwise noted, all content on this page is © Cengage Learning.

the freezing and boiling points of water are now defined as 32°F and 212°F, respectively. In scientific work, temperatures are often expressed on the **Kelvin** (absolute) temperature scale. As we shall see in Section 12-5, the zero point of the Kelvin temperature scale is derived from the observed behavior of all matter.

Relationships among the three temperature scales are illustrated in Figure 1-20. Between the freezing point of water and the boiling point of water, there are 100 steps (°C or kelvins, respectively) on the Celsius and Kelvin scales. Thus the “degree” is the same size on the Celsius and Kelvin scales. But every Kelvin temperature is 273.15 units above the corresponding Celsius temperature. The relationship between these two scales is as follows:

► We will usually round 273.15 to 273.

$$\text{K} = ^\circ\text{C} + 273.15^\circ \quad \text{or} \quad ^\circ\text{C} = \text{K} - 273.15^\circ$$

In the SI system, “degrees Kelvin” are abbreviated simply as K rather than °K and are called **kelvins**.

Any temperature *change* has the same numerical value whether expressed on the Celsius scale or on the Kelvin scale. For example, a change from 25°C to 59°C represents a *change* of 34 Celsius degrees. Converting these to the Kelvin scale, the same change is expressed as $(273 + 25) = 298$ K to $(59 + 273) = 332$ K, or a *change* of 34 kelvins.

Comparing the Fahrenheit and Celsius scales, we find that the intervals between the same reference points are 180 Fahrenheit degrees and 100 Celsius degrees, respectively. Thus a Fahrenheit degree must be smaller than a Celsius degree. It takes 180 Fahrenheit degrees to cover the same temperature *interval* as 100 Celsius degrees. From this information, we can construct the unit factors for temperature *changes*:

► The numbers in these ratios are exact numbers, so they do not affect the number of significant figures in the calculated result.

$$\frac{180^\circ\text{F}}{100^\circ\text{C}} \quad \text{or} \quad \frac{1.8^\circ\text{F}}{1.0^\circ\text{C}} \quad \text{and} \quad \frac{100^\circ\text{C}}{180^\circ\text{F}} \quad \text{or} \quad \frac{1.0^\circ\text{C}}{1.8^\circ\text{F}}$$

But the starting points of the two scales are different, so we *cannot convert* a temperature on one scale to a temperature on the other just by multiplying by the unit factor. In converting from °F to °C, we must also subtract 32 Fahrenheit degrees to reach the zero point on the Celsius scale (see Figure 1-20).

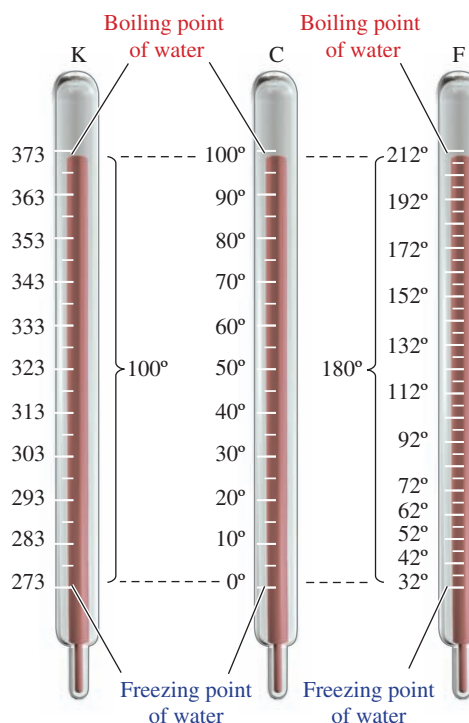


Figure 1-20 The relationships among the Kelvin, Celsius (centigrade), and Fahrenheit temperature scales.

$$\underline{x}^{\circ}\text{C} = \frac{1.0^{\circ}\text{C}}{1.8^{\circ}\text{F}} (x^{\circ}\text{F} - 32^{\circ}\text{F}) \quad \text{or} \quad \underline{x}^{\circ}\text{F} = \left(x^{\circ}\text{C} \times \frac{1.8^{\circ}\text{F}}{1.0^{\circ}\text{C}} \right) + 32^{\circ}\text{F}$$

► These are often remembered in abbreviated form:

$$\begin{aligned} ^{\circ}\text{C} &= \frac{(^{\circ}\text{F} - 32^{\circ})}{1.8} \\ ^{\circ}\text{F} &= 1.8^{\circ}\text{C} + 32^{\circ} \end{aligned}$$

Either of these equations can be rearranged to obtain the other one, so you need to learn only one of them.

EXAMPLE 1-16 Temperature Conversion

When the temperature reaches “100. °F in the shade,” it’s hot. What is this temperature on the Celsius scale?

Plan

We use the relationship $\underline{x}^{\circ}\text{C} = \frac{1.0^{\circ}\text{C}}{1.8^{\circ}\text{F}} (x^{\circ}\text{F} - 32^{\circ}\text{F})$ to carry out the desired conversion.

Solution

$$\underline{x}^{\circ}\text{C} = \frac{1.0^{\circ}\text{C}}{1.8^{\circ}\text{F}} (100.^{\circ}\text{F} - 32^{\circ}\text{F}) = \frac{1.0^{\circ}\text{C}}{1.8^{\circ}\text{F}} (68^{\circ}\text{F}) = 38^{\circ}\text{C}$$

► A temperature of 100.°F is 38°C.

EXAMPLE 1-17 Temperature Conversion

When the absolute temperature is 400 K, what is the Fahrenheit temperature?

Plan

We first use the relationship $\underline{x}^{\circ}\text{C} = \text{K} - 273^{\circ}$ to convert from kelvins to degrees Celsius; then we carry out the further conversion from degrees Celsius to degrees Fahrenheit.

Solution

$$\begin{aligned} \underline{x}^{\circ}\text{C} &= (400\text{ K} - 273\text{ K}) \frac{1.0^{\circ}\text{C}}{1.0\text{ K}} = 127^{\circ}\text{C} \\ \underline{x}^{\circ}\text{F} &= \left(127^{\circ}\text{C} \times \frac{1.8^{\circ}\text{F}}{1.0^{\circ}\text{C}} \right) + 32^{\circ}\text{F} = 261^{\circ}\text{F} \end{aligned}$$

You should now work Exercise 54.

1-13 Heat Transfer and the Measurement of Heat

Chemical reactions and physical changes occur with either the simultaneous evolution of heat (**exothermic processes**) or the absorption of heat (**endothermic processes**). The amount of heat transferred in a process is usually expressed in joules or in calories.

The SI unit of energy and work is the **joule (J)**, which is defined as $1\text{ kg} \cdot \text{m}^2/\text{s}^2$. The kinetic energy (KE) of a body of mass m moving at speed v is given by $\frac{1}{2}mv^2$. A 2-kg object moving at one meter per second has $\text{KE} = \frac{1}{2}(2\text{ kg})(1\text{ m/s})^2 = 1\text{ kg} \cdot \text{m}^2/\text{s}^2 = 1\text{ J}$. You may find it more convenient to think in terms of the amount of heat required to raise the temperature of one gram of liquid water from 14.5°C to 15.5°C, which is 4.184 J.

One **calorie** is defined as exactly 4.184 J. The so-called “large calorie,” used to indicate the energy content of foods, is really one kilocalorie, that is, 1000 calories. In this text, we shall do most calculations in joules.

The **specific heat** of a substance is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius (also one kelvin) with no change in phase. Changes in phase (physical state) absorb or liberate relatively large amounts of

► In terms of electrical energy, one joule is equal to one watt · second. Thus, one joule is enough energy to operate a 10-watt light bulb for $\frac{1}{10}$ second.

Unless otherwise noted, all content on this page is © Cengage Learning.

► The calorie was originally defined as the amount of heat necessary to raise the temperature of one gram of water at one atmosphere from 14.5°C to 15.5°C.

► The specific heat of a substance varies *slightly* with temperature and pressure. These variations can be ignored for calculations in this text.

energy (see Figure 1-5). The specific heat of each substance, a physical property, is different for the solid, liquid, and gaseous phases of the substance. For example, the specific heat of ice is 2.09 J/g · °C near 0°C; for liquid water it is 4.18 J/g · °C; and for steam it is 2.03 J/g · °C near 100°C. The specific heat for water is quite high. A table of specific heats is provided in Appendix E.

$$\text{specific heat} = \frac{(\text{amount of heat in J})}{(\text{mass of substance in g})(\text{temperature change in } ^\circ\text{C})}$$

The units of specific heat are $\frac{\text{J}}{\text{g} \cdot ^\circ\text{C}}$ or $\text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$.

The **heat capacity** of a body is the amount of heat required to raise its temperature 1°C. The heat capacity of a body is its mass in grams times its specific heat. The heat capacity refers to the mass of that particular body, so its units do not include mass. The units are J/°C or J · °C⁻¹.

► In this example, we calculate the amount of heat needed to prepare a cup of hot tea.

EXAMPLE 1-18 Specific Heat

How much heat, in joules, is required to raise the temperature of 205 g of water from 21.2°C to 91.4°C?

Plan

The specific heat of a substance is the amount of heat required to raise the temperature of 1 g of the substance by 1°C:

$$\text{specific heat} = \frac{(\text{amount of heat in J})}{(\text{mass of substance in g})(\text{temperature change in } ^\circ\text{C})}$$

We can rearrange the equation so that

$$(\text{amount of heat}) = (\text{mass of substance})(\text{specific heat})(\text{temperature change})$$

Alternatively, we can use the unit factor approach.

Solution

$$\text{amount of heat} = (205 \text{ g})(4.18 \text{ J/g} \cdot ^\circ\text{C})(70.2^\circ\text{C}) = 6.02 \times 10^4 \text{ J}$$

By the unit factor approach,

$$\text{amount of heat} = (205 \text{ g}) \left(\frac{4.18 \text{ J}}{1 \text{ g} \cdot ^\circ\text{C}} \right) (70.2^\circ\text{C}) = 6.02 \times 10^4 \text{ J} \quad \text{or} \quad 60.2 \text{ kJ}$$

All units except joules cancel. To cool 205 g of water from 91.4°C to 21.2°C, it would be necessary to remove exactly the same amount of heat, 60.2 kJ.

You should now work Exercises 62 and 63.

When two objects at different temperatures are brought into contact, heat flows from the hotter to the colder body (Figure 1-21); this continues until the two are at the same temperature. We say that the two objects are then in *thermal equilibrium*. The temperature change that occurs for each object depends on the initial temperatures and the relative masses and specific heats of the two materials.



Charles D. Winters

A Heat is transferred from the hotter metal bar to the cooler water until the two reach the same temperature.



B We say that they are then at *thermal equilibrium*.

Figure 1-21 A hot object, such as a heated piece of metal, is placed into cooler water.

EXAMPLE 1-19 Specific Heat

A 588-gram chunk of iron is heated to 97.5°C. Then it is immersed in 247 grams of water originally at 20.7°C. When thermal equilibrium has been reached, the water and iron are both at 36.2°C. Calculate the specific heat of iron.

Plan

The amount of heat gained by the water as it is warmed from 20.7°C to 36.2°C is the same as the amount of heat lost by the iron as it cools from 97.5°C to 36.2°C. We can equate these two amounts of heat and solve for the unknown specific heat.

Solution

$$\text{temperature change of water} = 36.2^\circ\text{C} - 20.7^\circ\text{C} = 15.5^\circ\text{C}$$

$$\text{temperature change of iron} = 97.5^\circ\text{C} - 36.2^\circ\text{C} = 61.3^\circ\text{C}$$

$$\text{number of joules gained by water} = (247 \text{ g}) \left(4.18 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) (15.5^\circ\text{C})$$

Let x = specific heat of iron

$$\text{number of joules lost by iron} = (588 \text{ g}) \left(x \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) (61.3^\circ\text{C})$$

We set these two quantities equal to one another and solve for x .

$$(247 \text{ g}) \left(4.18 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) (15.5^\circ\text{C}) = (588 \text{ g}) \left(x \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) (61.3^\circ\text{C})$$

$$x = \frac{(247 \text{ g}) \left(4.18 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) (15.5^\circ\text{C})}{(588 \text{ g}) (61.3^\circ\text{C})} = 0.444 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}}$$

You should now work Exercise 66.

► In specific heat calculations, we use the *magnitude* of the temperature change (i.e., a positive number), so we subtract the lower temperature from the higher one in both cases.

The specific heat of iron is much smaller than the specific heat of water.

$$\frac{\text{specific heat of iron}}{\text{specific heat of water}} = \frac{0.444 \text{ J/g} \cdot ^\circ\text{C}}{4.18 \text{ J/g} \cdot ^\circ\text{C}} = 0.106$$

The amount of heat required to raise the temperature of 205 g of iron by 70.2°C (as we calculated for water in Example 1-18) is

$$\text{amount of heat} = (205 \text{ g}) \left(\frac{0.444 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \right) (70.2^\circ\text{C}) = 6.39 \times 10^3 \text{ J, or } 6.39 \text{ kJ}$$

We see that the amount of heat required to accomplish a given change in temperature for a given quantity of iron is less than that for the same quantity of water, by the same ratio.

$$\frac{\text{number of joules required to warm 205 g of iron by } 70.2^\circ\text{C}}{\text{number of joules required to warm 205 g of water by } 70.2^\circ\text{C}} = \frac{6.39 \text{ kJ}}{60.2 \text{ kJ}} = 0.106$$

It might not be necessary to carry out explicit calculations when we are looking only for qualitative comparisons.

EXAMPLE 1-20 Comparing Specific Heats

We add the same amount of heat to 10.0 grams of each of the following substances starting at 20.0°C: liquid water, $\text{H}_2\text{O}(\ell)$; liquid mercury, $\text{Hg}(\ell)$; liquid benzene, $\text{C}_6\text{H}_6(\ell)$; and solid aluminum, $\text{Al}(\text{s})$. Rank the samples from lowest to highest final temperature. Refer to Appendix E for required data.

Plan

We can obtain the values of specific heats (Sp. Ht.) for these substances from Appendix E. The higher the specific heat for a substance, the more heat is required to raise a given mass of sample by a given temperature change, so the less its temperature changes by a given amount of heat. The substance with the lowest specific heat undergoes the largest temperature change, and the one with the highest specific heat undergoes the smallest temperature change. *It is not necessary to calculate the amount of heat required to answer this question.*

Solution

The specific heats obtained from Appendix E are as follows:

Substance	Sp. Ht. $\left(\frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right)$
$\text{H}_2\text{O}(\ell)$	4.18
$\text{Hg}(\ell)$	0.138
$\text{C}_6\text{H}_6(\ell)$	1.74
$\text{Al}(\text{s})$	0.900

Ranked from highest to lowest specific heats: $\text{H}_2\text{O}(\ell) > \text{C}_6\text{H}_6(\ell) > \text{Al}(\text{s}) > \text{Hg}(\ell)$. Adding the same amount of heat to the same size sample of these substances changes the temperature of $\text{H}_2\text{O}(\ell)$ the least and that of $\text{Hg}(\ell)$ the most. The ranking from lowest to highest final temperature is

$$\text{H}_2\text{O}(\ell) < \text{C}_6\text{H}_6(\ell) < \text{Al}(\text{s}) < \text{Hg}(\ell)$$

You should now work Exercise 75.

KEY TERMS

Accuracy How closely a measured value agrees with the correct value (see Appendix A-4).

Atom The smallest particle of an element that maintains its chemical identity through all chemical and physical changes.

Atomic number The number of protons in the nucleus of an atom.

Calorie Defined as exactly 4.184 joules. Originally defined as the amount of heat required to raise the temperature of one gram of water from 14.5°C to 15.5°C.

Chemical change A change in which one or more new substances are formed; also known as *chemical reaction* or just *reaction*.

Chemical property See *Properties*.

Compound A substance composed of two or more elements in fixed proportions. Compounds can be decomposed into their constituent elements.

Density Mass per unit volume, $D = m/V$.

Element A substance that cannot be decomposed into simpler substances by chemical means.

Endothermic Describes processes that absorb heat energy.

Energy The capacity to do work or transfer heat.

Exothermic Describes processes that release heat energy.

Extensive property A property that depends on the amount of material in a sample.

Heat A form of energy that flows between two samples of matter because of their difference in temperature.

Heat capacity The amount of heat required to raise the temperature of a body one degree Celsius.

Heterogeneous mixture A mixture that does not have uniform composition and properties throughout.

Homogeneous mixture A mixture that has uniform composition and properties throughout.

Intensive property A property that is independent of the amount of material in a sample.

Joule A unit of energy in the SI system. One joule is $1 \text{ kg} \cdot \text{m}^2/\text{s}^2$, which is also 0.2390 cal.

Kinetic energy Energy that matter possesses by virtue of its motion.

Law of Conservation of Energy Energy cannot be created or destroyed in a chemical reaction or in a physical change; it may be changed from one form to another.

Law of Conservation of Matter No detectable change occurs in the total quantity of matter during a chemical reaction or during a physical change.

Law of Conservation of Matter and Energy The combined amount of matter and energy in the universe is fixed.

Law of Constant Composition See *Law of Definite Proportions*.

Law of Definite Proportions Different samples of any pure compound contain the same elements in the same proportions by mass; also known as the *Law of Constant Composition*.

Mass A measure of the amount of matter in an object. Mass is usually measured in grams or kilograms.

Matter Anything that has mass and occupies space.

Mixture A sample of matter composed of variable amounts of two or more substances, each of which retains its identity and properties.

Molecule The smallest particle of an element or compound that can have a stable independent existence.

Physical change A change in which a substance changes from one physical state to another, but no substances with different compositions are formed.

Physical property See *Properties*.

Potential energy Energy that matter possesses by virtue of its position, condition, or composition.

Precision How closely repeated measurements of the same quantity agree with one another (see Appendix A-4).

Properties Characteristics that describe samples of matter. Chemical properties are exhibited as matter undergoes chemical changes. Physical properties are exhibited by matter with no changes in chemical composition.

Scientific (natural) law A general statement based on the observed behavior of matter, to which no exceptions are known.

Significant figures Digits that indicate the precision of measurements—digits of a measured number that have uncertainty only in the last digit (see Appendix A-4).

Specific gravity The ratio of the density of a substance to the density of water at the same temperature.

Specific heat The amount of heat required to raise the temperature of one gram of a substance by one degree Celsius.

Substance Any kind of matter all specimens of which have the same chemical composition and physical properties.

Symbol (of an element) A letter or group of letters that represents (identifies) an element.

Temperature A measure of the intensity of heat, that is, the hotness or coldness of a sample or object.

Unit factor A factor in which the numerator and denominator are expressed in different units but represent the same or equivalent amounts. Multiplying by a unit factor is the same as multiplying by one.

Weight A measure of the gravitational attraction of the earth for a body.

EXERCISES

● Molecular Reasoning exercises

▲ More Challenging exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Matter and Energy

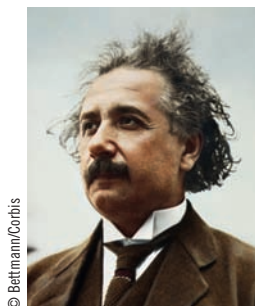
1. Define the following subdivisions of chemistry: (a) biochemistry; (b) analytical chemistry; (c) geochemistry; (d) nuclear chemistry; (e) inorganic chemistry. (*Hint:* You may need to consult a dictionary for answers to this question.)
2. Define the following subdivisions of chemistry: (a) organic chemistry; (b) forensic chemistry; (c) physical chemistry; (d) medicinal chemistry. (*Hint:* You may need to consult a dictionary for answers to this question.)
3. Define the following terms, and illustrate each with a specific example: (a) matter; (b) kinetic energy; (c) mass; (d) exothermic process; (e) intensive property.
4. Define the following terms, and illustrate each with a specific example: (a) weight; (b) potential energy; (c) temperature; (d) endothermic process; (e) extensive property.
5. State the Law of Conservation of Matter and Energy, and explain how it differs from the Law of Conservation of Matter and the Law of Conservation of Energy.
6. Describe why you can refer to the following processes as being exothermic even though very little or no heat is being released: (a) discharge of a flashlight battery; (b) the production of light by an activated light stick.
7. Describe why you can refer to the following processes as being exothermic even though very little or no heat is being released: (a) the production of light by a fluorescent light; (b) the production of light by a glow-in-the-dark object.
8. Which of the following processes are exothermic? endothermic? How can you tell? (a) combustion; (b) freezing water; (c) melting ice; (d) boiling water; (e) condensing steam; (f) burning paper.
9. Which of the following processes are exothermic? endothermic? How can you tell? (a) burning gasoline; (b) freezing ice cream; (c) melting chocolate; (d) cooling hot water; (e) condensing water vapor; (f) burning a match.
10. Write Einstein's equation, and describe how it can be used to relate the mass change in a nuclear reaction to energy.
11. State the following laws, and illustrate each: (a) the Law of Conservation of Matter; (b) the Law of Conservation of Energy; (c) the Law of Conservation of Matter and Energy.
12. All electrical motors are less than 100% efficient in converting electrical energy into useable work. How can their efficiency be less than 100% and the Law of Conservation of Energy still be valid?
13. An incandescent light bulb functions because of the flow of electric current. Does the incandescent light bulb convert all of the electrical energy to light? Observe a functioning incandescent light bulb, and explain what occurs with reference to the Law of Conservation of Energy.

States of Matter

14. ● List the three states of matter and some characteristics of each. How are they alike? Different? Draw a molecular representation that illustrates differences in the amount of space between molecules in the gaseous and the liquid or solid states.
15. What is a homogeneous mixture? Which of the following are pure substances? Which of the following are homogeneous mixtures? Explain your answers: (a) salt dissolved in water; (b) tea and ice; (c) chicken noodle soup; (d) mud; (e) gasoline; (f) carbon dioxide; (g) mint chocolate-chip ice cream.



© Danilo Calilung/Corbis



© Bettmann/Corbis

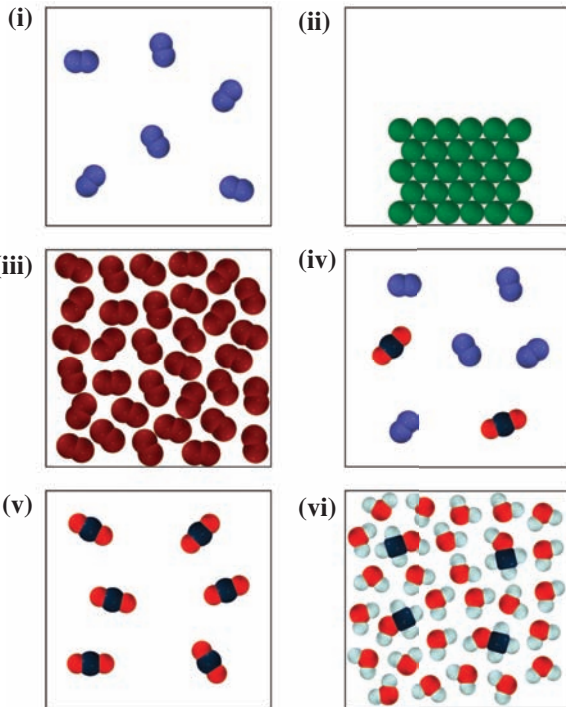
● Molecular Reasoning exercises

▲ More Challenging exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

16. Define the following terms clearly and concisely. Give two examples of each: (a) substance; (b) mixture; (c) element; (d) compound.

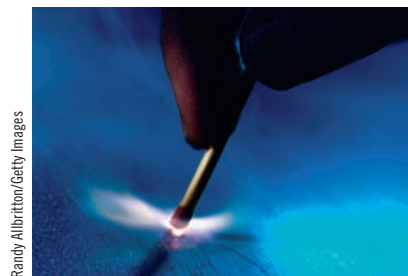


17. The preceding boxes include models of (a) a gaseous element; (b) a gaseous compound; (c) a homogeneous gaseous mixture; (d) a liquid solution; (e) a solid; (f) a pure liquid. Identify each type and provide other examples of each type. Explain your answers.
18. Classify each of the following as an element, a compound, or a mixture. Justify your classification: (a) gasoline; (b) tap water; (c) calcium carbonate; (d) ink from a ballpoint pen; (e) vegetable soup; (f) aluminum foil.
19. What experiment can you use to (a) separate salt from water? (b) separate iron filings from small pieces of lead? (c) separate elemental sulfur from sugar?
20. A \$10 gold piece minted in the early 1900s appeared to have a dirty area. The dirty appearance could not be removed by careful cleaning. Close examination of the coin revealed that the “dirty” area was really pure copper. Is the mixture of gold and copper in this coin a heterogeneous or homogeneous mixture?

Chemical and Physical Properties

21. Distinguish between the following pairs of terms, and give two specific examples of each: (a) chemical properties and physical properties; (b) intensive properties and extensive properties; (c) chemical changes and physical changes; (d) mass and weight.
22. Which of the following are chemical properties, and which are physical properties? (a) striking a match

causes it to burst into flames; (b) a particular type of steel is very hard and consists of 95% iron, 4% carbon, and 1% other elements; (c) the density of gold is 19.3 g/mL; (d) baking soda dissolves in water and releases gaseous carbon dioxide; (e) fine steel wool burns in air; (f) refrigeration slows the rate at which fruit ripens.



23. Label each of the following as either a physical process or a chemical process: (a) rusting of an iron nail; (b) melting of ice; (c) burning of a wooden stick; (d) digestion of a baked potato; (e) dissolving of sugar in water.
24. Eight observations are listed below. What observations identify chemical properties?
- Sugar is soluble in water.
 - Water boils at 100°C.
 - Ultraviolet light converts O₃ (ozone) to O₂ (oxygen).
 - Ice is less dense than water.
 - Sodium metal reacts violently with water.
 - CO₂ does not support combustion.
 - Chlorine is a green gas.
 - Heat is required to melt ice.
25. Which of the following illustrate the concept of potential energy, and which illustrate kinetic energy? (a) a car moving at 55 miles per hour; (b) a rubber band stretched around a newspaper; (c) a frozen pint of ice cream; (d) a comet moving through space; (e) a basketball dropping through a net; (f) the roof of a house.
26. Which of the following illustrate the concept of potential energy, and which illustrate kinetic energy? (a) a moving car; (b) an inflated balloon; (c) a pitched baseball just as it is being released by the pitcher; (d) a flashlight battery; (e) a frozen lake; (f) a car as it moves along the highway.
27. Tongs are used to hold a sugar cube in a flame. When a portion of the cube begins to turn brown, the cube is removed from the flame. After cooling, the heated portion of the cube is brown and has a burnt aroma. Analysis tells us that the cube lost mass. Is the browning of the sugar a chemical or a physical change? Propose an explanation for these observations.
28. A weighed sample of yellow sulfur is placed in a flask. The flask is gently heated using a Bunsen burner. Observation indicates that nothing appears to happen to the sulfur during the heating, but the mass of sulfur is less than before the heating, and there is a sharp odor that was not present before the heating. Propose an explanation of what caused the change in the mass



of the sulfur. Is your hypothesis of the mass change a chemical or physical change?



Charles D. Winters

Sulfur

Measurements and Calculations

29. Express the following numbers in scientific notation: (a) 650.; (b) 0.0630; (c) 8600 (assume that this number is measured to 10); (d) 8600 (assume that this number is measured to 1); (e) 16,000.; (f) 0.100010.
30. For each of the following quantities, underline the zeros that are significant figures, determine the number of significant figures in the quantity, and rewrite the quantity using scientific notation: (a) 423.006 mL; (b) 0.001073040 g; (c) 1,081.02 pounds.
31. Which of the following are likely to be exact numbers? Why? (a) 128 students; (b) 7 railroad cars; (c) \$20,355.47; (d) 25 lb of sugar; (e) 12.5 gal of diesel fuel; (f) 5446 ants.
32. Express the following exponentials as ordinary numbers: (a) 5.06×10^4 ; (b) 4.060×10^{-4} ; (c) 16.10×10^{-2} ; (d) 0.206×10^{-3} ; (e) 9.000×10^4 ; (f) 9.000×10^{-4} .
33. The circumference of a circle is given by πd , where d is the diameter of the circle. Calculate the circumference of a circle with a diameter of 7.41 cm. Use the value of 3.141593 for π . (Show your answer with the correct number of significant figures.)
34. A box is 252.56 cm wide, 18.23 cm deep, and 6.5 cm tall. Calculate the volume of the box. (Show your answer with the correct number of significant figures.)
35. Indicate the multiple or fraction of 10 by which a quantity is multiplied when it is preceded by each of the following prefixes. (a) M; (b) m; (c) c; (d) d; (e) k; (f) n.
36. Carry out each of the following conversions: (a) 453.4 m to km; (b) 36.3 km to m; (c) 487 kg to g; (d) 1.32 L to mL; (e) 55.9 dL to L; (f) 6251 L to cm^3 .
37. Express 5.31 centimeters in meters, millimeters, kilometers, and micrometers.
38. If the price of gasoline is \$3.119/gal, what is its price in cents per liter?
39. Suppose your automobile gas tank holds 14 gal and the price of gasoline is \$0.861/L. How much would it cost to fill your gas tank?
40. Express (a) 0.750 cubic foot in units of liters; (b) 1.00 liter in units of pints; (c) miles per gallon in kilometers per liter.
41. The screen of a netbook computer measures 8.25 in. wide and 6.25 in. tall. If this computer were being sold in Europe, what would be the metric size, in cm, of the screen used in the specifications for the computer?
42. Two students ran the same reaction. One student obtained 58.2% yield. The other student, using a different type of balance, obtained 56.474% yield. What is the average of their percent yields? (Show your answer with the correct number of significant figures.)
43. Calculate the total mass of three samples that have the masses of 10.25 g, 5.5654 g, and 105.4 g. (Show your answer with the correct number of significant figures.)
44. Do each of the following calculations and give the answer in the correct units and number of significant figures: (a) $18 \text{ pints} \times 1 \text{ qt}/2 \text{ pints}$; (b) $55.0 \text{ miles per hour} \times 1.609 \text{ km/mile}$; (c) $15.45 \text{ seconds} + 2.2 \text{ seconds} + 55 \text{ seconds}$.
45. What is the mass of a rectangular piece of copper $24.4 \text{ cm} \times 11.4 \text{ cm} \times 7.9 \text{ cm}$? The density of copper is 8.92 g/cm^3 .
46. A small crystal of sucrose (table sugar) had a mass of 6.080 mg. The dimensions of the box-like crystal were $2.20 \text{ mm} \times 1.36 \text{ mm} \times 1.23 \text{ mm}$. What is the density of sucrose expressed in g/cm^3 ?
47. Vinegar has a density of 1.0056 g/cm^3 . What is the mass of three liters of vinegar?
48. The density of silver is 10.5 g/cm^3 . (a) What is the volume, in cm^3 , of an ingot of silver with mass 0.443 kg? (b) If this sample of silver is a cube, how long is each edge in cm? (c) How long is the edge of this cube in inches?



Alex Wilson/Getty Images



Charles D. Winters

49. ▲ A container has a mass of 78.91 g when empty and 92.44 g when filled with water. The density of water is 1.0000 g/cm^3 . (a) Calculate the volume of the container. (b) When filled with an unknown liquid, the container had a mass of 88.42 g. Calculate the density of the unknown liquid.
50. ▲ Wire is often sold in pound spools according to the wire gauge number. That number refers to the diameter of the wire. How many meters are in a 10-lb spool of 12-gauge aluminum wire? A 12-gauge wire has a diameter of 0.0808 in. Aluminum has a density of 2.70 g/cm^3 . ($V = \pi r^2 \ell$)
51. A solution is 40.0% acetic acid (the characteristic component in vinegar) by mass. The density of this solution is 1.049 g/mL at 20°C . Calculate the mass of pure acetic acid in 250.0 mL of this solution at 20°C .
52. A solution that is 11% iron(III) chloride by mass has a density of 1.149 g/mL . What mass of iron(III) chloride, in g, is present in 2.50 L of this solution?

Heat Transfer and Temperature Measurement

53. Express (a) 245°C in K; (b) 25.2 K in $^\circ\text{C}$; (c) -42.0°C in $^\circ\text{F}$; (d) 110.0°F in K.
54. Express (a) 15°F in $^\circ\text{C}$; (b) 32.6°F in K; (c) 328 K in $^\circ\text{F}$; (d) 11.3°C in $^\circ\text{F}$.
55. Which temperature is higher? (a) 20°C or 20°F ; (b) 100°C or 180°F ; (c) 60°C or 100°F ; (d) -12°C or 20°F .
56. ▲ On the Réaumur scale, which is no longer used, water freezes at 0°R and boils at 80°R . (a) Derive an equation that relates this to the Celsius scale. (b) Derive an equation that relates this to the Fahrenheit scale. (c) Mercury is a liquid metal at room temperature. It boils at 356.6°C (673.9°F). What is the boiling point of mercury on the Réaumur scale?
57. Liquefied gases have boiling points well below room temperature. On the Kelvin scale the boiling points of the following gases are: He, 4.2 K ; N_2 , 77.4 K . Convert these temperatures to the Celsius and the Fahrenheit scales.
58. Convert the temperatures at which the following metals melt to the Celsius and Fahrenheit scales: Al, 933.6 K ; Ag, 1235.1 K .
59. At what point is the temperature in $^\circ\text{F}$ exactly twice that in $^\circ\text{C}$?
60. The average temperature of a healthy German shepherd is 102.0°F . Express this temperature (a) in degrees Celsius; (b) in kelvins.
61. Calculate the amount of heat required to raise the temperature of 78.2 g of water from 10.0°C to 32.0°C . The specific heat of water is $4.184 \text{ J/g} \cdot ^\circ\text{C}$.
62. The specific heat of aluminum is $0.895 \text{ J/g} \cdot ^\circ\text{C}$. Calculate the amount of heat required to raise the temperature of 45.3 g of aluminum from 27.0°C to 62.5°C .
63. How much heat must be removed from 15.5 g of water at 90.0°C to cool it to 38.2°C ?
64. ▲ In some solar-heated homes, heat from the sun is stored in rocks during the day and then released during the cooler night. (a) Calculate the amount of heat required to raise the temperature of 69.7 kg of rocks from 25.0°C to 41.0°C . Assume that the rocks are limestone, which is essentially pure calcium carbonate. The specific heat of calcium carbonate is $0.818 \text{ J/g} \cdot ^\circ\text{C}$. (b) Suppose that when the rocks in part (a) cool to 30.0°C , all the heat released goes to warm the $10,000 \text{ ft}^3$ ($2.83 \times 10^5 \text{ L}$) of air in the house, originally at 10.0°C . To what final temperature would the air be heated? The specific heat of air is $1.004 \text{ J/g} \cdot ^\circ\text{C}$, and its density is $1.20 \times 10^{-3} \text{ g/mL}$.
65. ▲ A small immersion heater is used to heat water for a cup of coffee. We wish to use it to heat 245 mL of water (about a teacupful) from 25°C to 85°C in 2.00 min. What must be the heat rating of the heater, in kJ/min , to accomplish this? Ignore the heat that goes to heat the cup itself. The density of water is 0.997 g/mL .
66. When 50.0 grams of metal at 75.0°C is added to $100. \text{ grams}$ of water at 15.0°C , the temperature of the water rises to 18.3°C . Assume that no heat is lost to the surroundings. What is the specific heat of the metal?

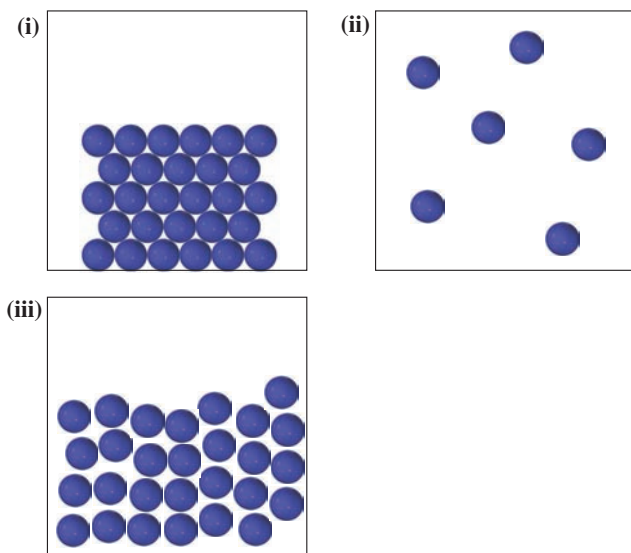
Mixed Exercises

67. A sample is marked as containing 25.8% calcium carbonate by mass. (a) How many grams of calcium carbonate are contained in 75.45 g of the sample? (b) How many grams of the sample would contain 18.8 g of calcium carbonate?
68. An iron ore is found to contain 9.24% hematite (a compound that contains iron). (a) How many tons of this ore would contain 5.79 tons of hematite? (b) How many kilograms of this ore would contain 6.40 kg of hematite?
69. ▲ The radius of a hydrogen atom is about $0.37 \text{ \AA}$, and the average radius of the earth's orbit around the sun is about $1.5 \times 10^8 \text{ km}$. Find the ratio of the average radius of the earth's orbit to the radius of the hydrogen atom.
70. A notice on a bridge informs drivers that the height of the bridge is 23.5 ft . How tall in meters is an 18-wheel tractor-trailer combination if it just touches the bridge?
71. Some American car manufacturers install speedometers that indicate speed in the English system and in the metric system (mi/h and km/h). What is the metric speed if the car is traveling at 65 mi/h ?
72. ▲ The lethal dose of a specific drug taken orally is 1.5 mg/kg of body weight. Calculate the lethal dose of the drug taken orally by a 165-lb person.
73. Suppose you ran a mile in 4.90 min . (a) What would be your average speed in km/h ? (b) What would be your average speed in cm/s ? (c) What would be your time (in minutes: seconds) for 1500 m ?
74. Household ammonia is 5% ammonia by mass and has a density of 1.006 g/mL . What volume of this solution must a person purchase to obtain 25.8 g of ammonia?



Conceptual Exercises

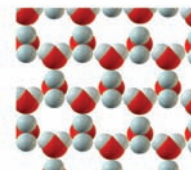
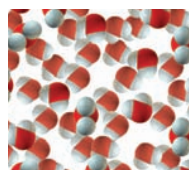
75. If you were given the job of choosing the materials from which pots and pans were to be made, what kinds of materials would you choose on the basis of specific heat? Why?
76. ● The following shows an element in each of its three physical states.



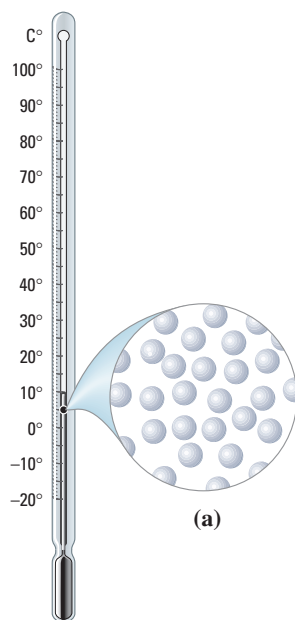
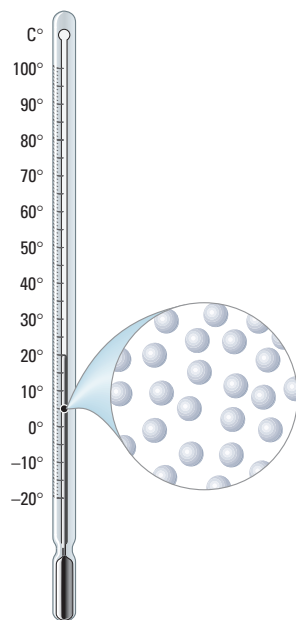
- (a) Which drawing represents a solid? (b) Which drawing represents a liquid? (c) Which drawing represents a gas? (d) Rank these physical states from least dense to most dense.
77. Although newly minted pennies look as though they are composed of copper, they actually contain only 2.7% copper. The remainder of the metal is zinc. If the

densities of copper and zinc are 8.72 g/cm^3 and 7.14 g/cm^3 respectively, what is the density of a newly minted penny?

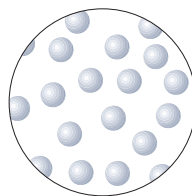
78. When she discovered that a piece of shiny gray zinc was too large to fit through the opening of an Erlenmeyer flask, a student cut the zinc into smaller pieces so they would fit. She then poured enough blue copper chloride solution into the flask to cover the zinc pieces. After 20 min the solution became colorless, the bottom of the flask was slightly warm to the touch, the zinc pieces were visibly reduced in size, and brown granular material appeared in the mixture. List the physical properties, physical changes, and chemical changes the student should have noted and recorded in her laboratory notebook.
79. Which is denser at 0°C , ice or water? How do you know?
80. ● Based upon the answer you gave for Exercise 79, which of the following drawings is a molecular representation for ice and which is for liquid water?



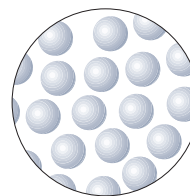
81. ● The drawing in the circle (at the bottom left) is a greatly expanded representation of the molecules in the liquid of the thermometer on its left. The thermometer registers 20°C . Which of the figures (a–d) is the best representation of the liquid in this same thermometer at 10°C ? (Assume that the same volume of liquid is shown in each expanded representation.)



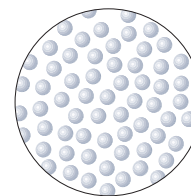
(a)



(b)

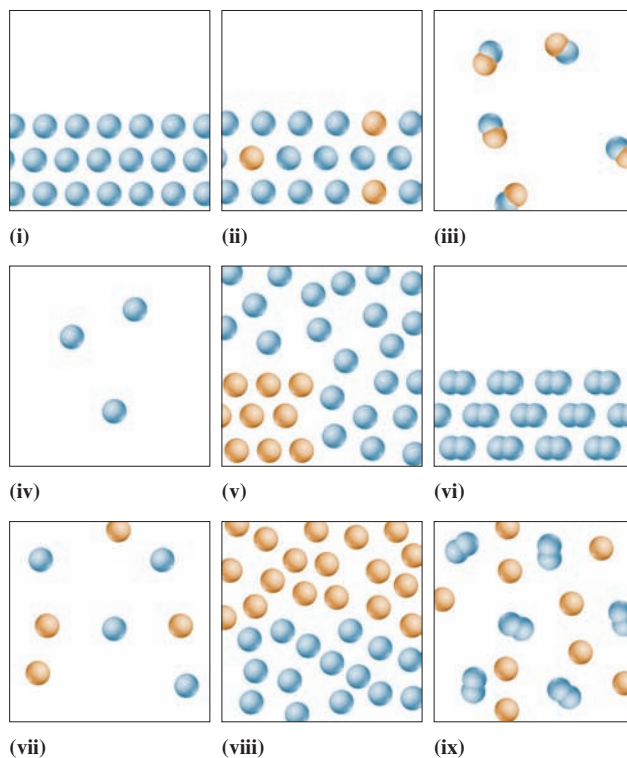


(c)

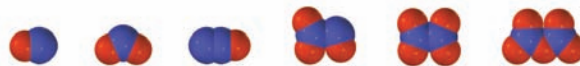


(d)

82. During the past several years, you have gained chemical vocabulary and understanding from a variety of academic and entertainment venues. List three events that occurred early in the development of your current chemical knowledge.
83. ▲ At what temperature will a Fahrenheit thermometer give (a) the same reading as a Celsius thermometer; (b) a reading that is twice that on the Celsius thermometer; (c) a reading that is numerically the same but opposite in sign from that on the Celsius thermometer?
84. ▲ Cesium atoms are the largest naturally occurring atoms. The radius of a cesium atom is $2.65 \text{ \AA}$. How many cesium atoms would have to be laid side by side to give a row of cesium atoms 1.00 in. long? Assume that the atoms are spherical.
85. Four balloons are each filled with a different gas of varying density:
 helium, $d = 0.164 \text{ g/L}$;
 neon, $d = 0.825 \text{ g/L}$;
 argon, $d = 1.633 \text{ g/L}$;
 krypton, $d = 4.425 \text{ g/L}$.
 If the density of dry air is 1.12 g/L , which balloon or balloons float in air?
86. As you write out the answer to an end-of-chapter exercise, what chemical changes occur? Did your answer involve knowledge not covered in Chapter 1?
87. *Combustion* is discussed later in this textbook; however, you probably already know what the term means. (Look it up to be sure.) List two other chemical terms that were in your vocabulary before you read Chapter 1.
88. Which has the higher temperature, a sample of water at 65°C or a sample of iron at 65°F ?
89. Answer the following questions using figures (i) to (ix). Each question may have more than one answer. (a) Which represents nanoscale particles in a sample of gas? (b) Which represents nanoscale particles in a sample of liquid? (c) Which represents nanoscale particles in a sample of solid? (d) Which represents nanoscale particles in a sample of an element? (e) Which represents nanoscale particles in a sample of a compound? (f) Which represents nanoscale particles in a sample of a mixture? (g) Which represents nanoscale particles in a sample of a pure substance?



90. When nitrogen (N_2) reacts with oxygen (O_2), several compounds can be produced: NO , NO_2 , N_2O , N_2O_3 , N_2O_4 , and N_2O_5 . If a nitrogen atom is represented by $\bullet$ and an oxygen atom is represented by $\circ$, identify by its formula each of the following oxides of nitrogen:



91. Draw models representing an atom of chlorine and a molecule of chlorine. How are they different? Draw models representing an atom of carbon and a molecule of methane. How is methane different from chlorine?
92. Draw models representing samples (several atoms or molecules) of sulfur and oxygen at room temperature. In what ways are the two elements alike? How are they different? Sulfur can combine chemically with oxygen to produce sulfur dioxide. Draw models representing samples of sulfur dioxide and a mixture of sulfur and oxygen. In what ways are the compound and the mixture alike? How are they different? Is the mixture homogeneous or heterogeneous?
93. Charcoal is wood that has been heated in the absence of oxygen to eliminate the volatile organic compounds, leaving carbon and minerals (ash). When charcoal burns, the carbon alone combines with oxygen in the air, producing carbon dioxide. The carbon is a black solid, while the oxygen and the carbon dioxide are both colorless gases. Is the change from solid, black carbon and colorless oxygen gas to colorless carbon dioxide gas a physical change or a chemical change? Why? Are



- the colors and the states of matter of these substances physical properties or chemical properties? Why?
94. When the volume of 53.275 g of copper ($D = 8.92 \text{ g/cm}^3$) is calculated ($V = \frac{m}{D} = \frac{53.275 \text{ g}}{8.92 \text{ g/cm}^3} = 5.97253 \text{ cm}^3$), the answer is rounded to 3 significant figures ($V = 5.97 \text{ cm}^3$). Use the uncertainties in the mass and the density, implied by the way the numbers are written, to justify the final answer. Is the “7” the first uncertain digit? Is it the “9” (2 significant figures)? Or could it be the “2” (4 significant figures)?
95. What’s wrong with each of the following measurements? “There’s an animal out in the hallway, and its length is 51.” “The width of this room is 7.36 bleams.”
96. Suppose you were to convert 3475 centimeters to miles. Using the relationships $2.54 \text{ cm} = 1 \text{ in.}$, $12 \text{ in.} = 1 \text{ ft.}$, and $5280 \text{ ft} = 1 \text{ mi.}$, you would arrive at the answer $0.021\,592\,649 \text{ mi.}$, which would then be rounded to $0.021\,59 \text{ mi.}$ (3475 cm has 4 significant figures). Using the relationships $100 \text{ cm} = 1 \text{ m}$, $1000 \text{ m} = 1 \text{ km}$, and $1.609 \text{ km} = 1 \text{ mi}$ (to 4 significant figures), you would arrive at the answer $0.021\,597\,265 \text{ mi.}$, which would then be rounded to $0.021\,60 \text{ mi.}$ Why aren’t the answers exactly the same? Is one of the relationships incorrect? Which calculation uses only exact relationships? Is the result of that calculation exact? Is it more accurate than the result of the other calculation?
97. The temperature of the surface of the sun (the photosphere) ranges from 5500°C to 6000°C . Convert 5500°C to kelvins and $^\circ\text{F}$. Suppose a famous astronomer, in a public lecture for the general public, said that the temperature of the surface of the sun is $10,000^\circ$. Would she be referring to the Celsius, Kelvin, or Fahrenheit temperature scale (or is she just confused)?
98. Amount of heat, specific heat, and temperature are such closely related properties of a substance that they are often confused. How are they related to each other? How are they different, by definition? One way to distinguish these three properties is by the unit used. What units might be used by a scientist for each of these properties?

Beyond the Textbook

NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.*

99. Use an internet search engine (such as <http://www.google.com>) to locate the total surface area of the state of Idaho. Report your answer in square meters. Repeat the search but this time for Ohio. How does the surface area of the two states compare?
100. Go to <http://www.google.com> or another internet search engine to locate the information needed to answer the following: (a) Which of the world’s oceans has the largest area? (b) What is the area of that ocean in square kilometers? (c) What is the area of that ocean in square miles?
101. Go to <http://www.google.com> or another internet search engine to locate the information needed to answer the following: (a) Which of the world’s oceans has the largest volume? (b) What is the volume of that ocean in cubic kilometers? (c) What is the volume of that ocean in cubic miles? (d) What is the volume of that ocean in gallons?
102. Go to chemistry.about.com/od/branchesofchemistry or another suitable internet site and locate the four central concerns (branches) of chemistry. List the four central concerns for chemistry.
103. Go to chemistry.about.com/od/branchesofchemistry or another suitable internet site and locate the description of one of the branches of chemistry. Define the branch of chemistry that you have selected.
104. The definition of the meter has changed several times. Use an internet search engine (such as <http://www.google.com>) to locate the origin and various earlier definitions of the meter. Comment on some advantages of the present definition compared to earlier ones.
105. (a) Since the copyright date (2010) of the 9th edition of this text, the discovery of element 117 has been verified. What is the currently accepted name for element 117? (b) During that time period, names for elements 112, 114, and 116 have been recommended by the IUPAC for approval. Give the current names and symbols for elements 112, 114, and 116; tell for what (or whom) each of these latter three elements is named and describe the origin of the name.

Chemical Formulas and Composition

Stoichiometry

2



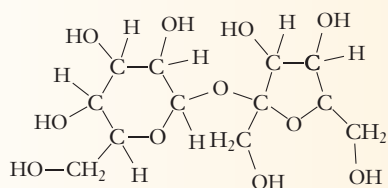
Rock candy is composed of large crystals of sucrose (sugar, $C_{12}H_{22}O_{11}$). A ball-and-stick model (C = black, O = red, H = white) of sucrose is superimposed on an electrostatic charge potential surface that shows the relative charges on the atoms (red = most negative, green = neutral, blue = most positive).

Courtesy of Dena Diglio Betz

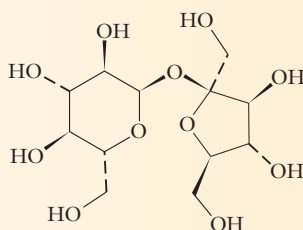
OUTLINE

- 2-1 Chemical Formulas
- 2-2 Ions and Ionic Compounds
- 2-3 Names and Formulas of Some Ionic Compounds
- 2-4 Atomic Weights
- 2-5 The Mole
- 2-6 Formula Weights, Molecular Weights, and Moles
- 2-7 Percent Composition and Formulas of Compounds
- 2-8 Derivation of Formulas from Elemental Composition
- 2-9 Determination of Molecular Formulas
- 2-10 Some Other Interpretations of Chemical Formulas
- 2-11 Purity of Samples

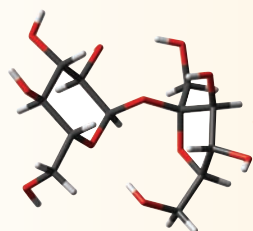
Four Different Representations of the Sucrose Molecule



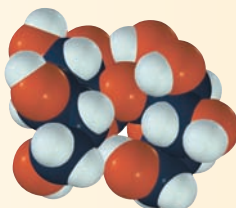
A Flat structural representation showing all atoms



B Organic line drawing using shorthand notation where carbon and attached hydrogen atoms are not indicated by their elemental symbols



C 3-D stick representation



D A space-filling model

Unless otherwise noted, all content on this page is © Cengage Learning.

OBJECTIVES

After you have studied this chapter, you should be able to

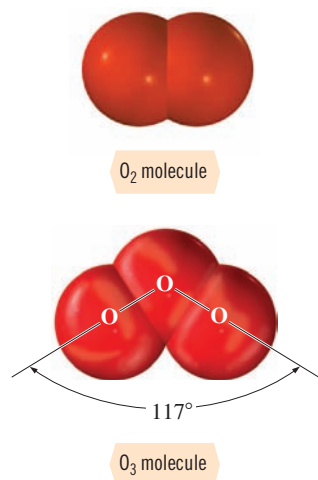
- ▶ Use chemical formulas to solve various kinds of chemical problems
- ▶ Relate names to formulas and charges of simple ions
- ▶ Combine simple ions to write formulas and names of some ionic compounds
- ▶ Recognize and use formula weights and mole relationships
- ▶ Interconvert masses, moles, and formulas
- ▶ Determine percent compositions in compounds
- ▶ Determine formulas from composition data
- ▶ Recognize models from calculated molecular formulas
- ▶ Perform calculations on the purity of substances

The language we use to describe the forms of matter and the changes in its composition is not limited to use in chemistry courses; it appears throughout the scientific world. Chemical symbols, formulas, and equations are used in such diverse areas as agriculture, home economics, engineering, geology, physics, biology, medicine, and dentistry. In this chapter we will use the simplest atomic theory as we represent the chemical formulas of elements and compounds. Later, after additional facts have been introduced, this theory will be expanded.

The word “stoichiometry” is derived from the Greek *stoicheion*, which means “first principle or element,” and *metron*, which means “measure.” **Stoichiometry** describes the quantitative relationships among elements in compounds (composition stoichiometry) and among substances as they undergo chemical changes (reaction stoichiometry). In this chapter we are concerned with chemical formulas and **composition stoichiometry**. In Chapter 3 we will discuss chemical equations and **reaction stoichiometry**.

2-1 Chemical Formulas

▶ It is important to learn this fundamental material well as it is the basis of all chemistry.



The **chemical formula** for a substance shows its chemical composition as elements present and the ratio in which the atoms of the elements occur. The formula for a single atom is the same as the symbol for the element. Thus, Na can represent a single sodium atom. It is quite unusual to find such isolated atoms in nature, with the exception of the noble gases (He, Ne, Ar, Kr, Xe, and Rn). A subscript following the symbol of an element indicates the number of atoms in a molecule. For instance, F_2 indicates a molecule containing two fluorine atoms, and P_4 a molecule containing four phosphorus atoms.

Some elements exist in more than one form. Familiar examples include (1) oxygen, found as O_2 molecules, and ozone, found as O_3 molecules, and (2) two crystalline forms of carbon—diamond and graphite (see Figure 13-32). Different structural forms of the same element are called **allotropic modifications**, or **allotropes**.

Compounds contain two or more elements in chemical combination in fixed proportions. Many compounds exist as molecules (Table 2-1). Hence, each molecule of hydrogen chloride, HCl, contains one atom of hydrogen and one atom of chlorine; each molecule of acetic acid, CH_3COOH , contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. Writing it as CH_3COOH (instead of $C_2H_4O_2$) includes useful bonding and structural information. An aspirin molecule, $C_9H_8O_4$, contains nine carbon atoms, eight hydrogen atoms, and four oxygen atoms.

Many of the molecules found in nature are organic compounds. **Organic compounds** contain C—C or C—H bonds or both, often in combination with nitrogen, oxygen, sulfur, and other elements. Eleven of the compounds listed in Table 2-1 are organic compounds (acetic acid and the last ten entries). All of the other compounds in the table are **inorganic compounds** (compounds that do not contain C—H bonds).

Some groups of atoms behave chemically as single entities. For instance, an oxygen atom that is bonded to a hydrogen atom and also to a carbon atom that is bonded to three other atoms forms the reactive combination of atoms known as the alcohol group or molecule. In

Table 2-1 Names and Formulas of Some Common Molecular Compounds

Name	Formula	Name	Formula	Name	Formula
water	H ₂ O	sulfur dioxide	SO ₂	butane	C ₄ H ₁₀
hydrogen peroxide	H ₂ O ₂	sulfur trioxide	SO ₃	pentane	C ₅ H ₁₂
hydrogen chloride*	HCl	carbon monoxide	CO	benzene	C ₆ H ₆
sulfuric acid	H ₂ SO ₄	carbon dioxide	CO ₂	methanol (methyl alcohol)	CH ₃ OH
nitric acid	HNO ₃	methane	CH ₄	ethanol (ethyl alcohol)	CH ₃ CH ₂ OH
acetic acid	CH ₃ COOH	ethane	C ₂ H ₆	acetone	CH ₃ COCH ₃
ammonia	NH ₃	propane	C ₃ H ₈	diethyl ether (ether)	CH ₃ CH ₂ OCH ₂ CH ₃

*Called hydrochloric acid if dissolved in water.

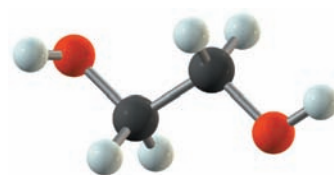
formulas of compounds containing two or more of the same group, the group formula is enclosed in parentheses. Thus C₂H₄(OH)₂ contains two *alcohol groups* (see margin); it is called ethylene glycol. When you count the number of atoms in this molecule from its formula, you must multiply the numbers of hydrogen and oxygen atoms in the OH group by 2. There are *two* carbon atoms, *six* hydrogen atoms and *two* oxygen atoms in a molecule of ethylene glycol. Thus, another way to write this formula is C₂H₆O₂, but this is not as informative to chemists (see Section 23-9).

Compounds were first recognized as distinct substances because of their different physical properties and because they could be separated from one another by physical methods. Once the concept of atoms and molecules was established, the reason for these differences in properties could be understood: Two compounds differ from each other because their molecules are different. Conversely, if two molecules contain the same number of the same kinds of atoms, arranged the same way, then both are molecules of the same compound. Thus, the atomic theory explains the **Law of Definite Proportions** (see Section 1-6).

This law, also known as the **Law of Constant Composition**, can now be extended to include its interpretation in terms of atoms. It is so important for performing the calculations in this chapter that we restate it here:

Different pure samples of a compound always contain the same elements in the same proportion by mass; this corresponds to atoms of these elements combined in fixed numerical ratios.

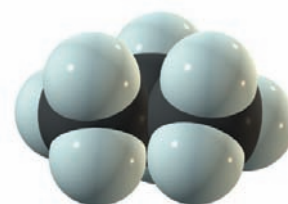
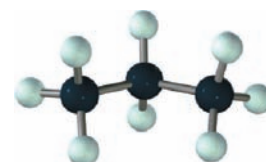
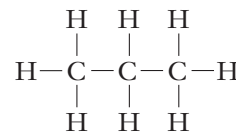
So we see that for a substance composed of molecules, the **chemical formula** gives the number of atoms of each type in the molecule. But this formula does not express the order in which the atoms in the molecules are bonded together. The **structural formula** shows the order in which atoms are connected. The lines connecting atomic symbols represent chemical bonds between atoms. The bonds are forces that tend to hold atoms at certain distances and angles from one another. For instance, the structural formula of propane, C₃H₈, shows that the three C atoms are linked in a chain, with three H atoms bonded to each of the end C atoms and two H atoms bonded to the center C. Chemists sometimes write out the formula in a way to better convey the connectivity information, e.g., CH₃CH₂CH₃, which is a longer representation of the propane chemical formula. Structural formulas are drawn flat and two-dimensional and do not usually indicate any specific three-dimensional information about the molecule. **Ball-and-stick** molecular models and **space-filling** molecular models help us to see the shapes and relative sizes of molecules. These four representations are shown in Figure 2-1. The ball-and-stick and space-filling models show (1) the *bonding sequence*, which is the order in which the atoms are connected to each other, and (2) the *geometrical arrangements* of the atoms in the molecule. As we will see later, both are extremely important because they determine the properties of compounds.



A Ball-and-stick model



B Space-filling model of ethylene glycol, the main constituent of automobile antifreeze



Unless otherwise noted, all content on this page is © Cengage Learning.

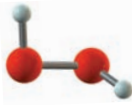
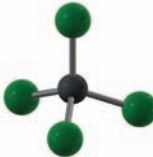
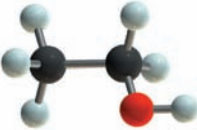
Chemical Formula	Structural Formula	Ball-and-Stick Model	Space-Filling Model
H ₂ O, water	H—O—H		
H ₂ O ₂ , hydrogen peroxide	H—O—O—H		
CCl ₄ , carbon tetrachloride	$ \begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array} $		
C ₂ H ₅ OH, ethanol	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array} $		

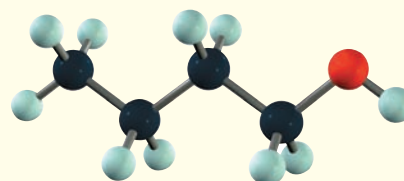
Figure 2-1 Formulas and models for some molecules. Structural formulas show the order in which atoms are connected but do not represent true molecular shapes. Ball-and-stick models use balls of different colors to represent atoms and sticks to represent bonds; they show the three-dimensional shapes of molecules. Space-filling models show the (approximate) relative sizes of atoms and the shapes of molecules, but the bonds between the atoms are hidden by the overlapping spheres that represent the atoms.

EXAMPLE 2-1 Chemical Formulas



Look at each of the following molecular models. For each one, write the structural formula and the chemical formula. (Color code: black = carbon; white = hydrogen; red = oxygen; blue = nitrogen; light green = fluorine; dark green = chlorine.)

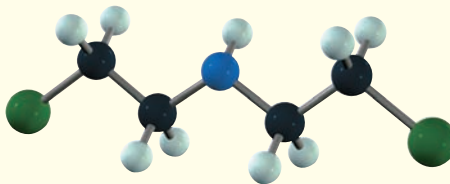
- (a) 1-butanol (occurs in some fruits, dried beans, cheese, and nuts; used as an additive in certain plastics, detergents, and some medicinal formulations)



- (b) Freon-12 (formerly used as a refrigerant; implicated in atmospheric ozone depletion)



- (c) nitrogen mustard HN1 (a highly toxic substance, used as a chemotherapy drug in the treatment of Hodgkin's disease and of some forms of chronic leukemia)

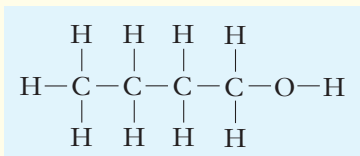


Plan

We identify each atom present from its color in the model. The structural formula shows which atoms are bonded to one another. We count the number of atoms of each type and represent the chemical formula with element symbols and subscripts, as described in this section.

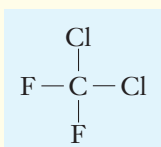
Solution

- (a) This ball-and-stick model shows that the atoms are bonded together as shown by the structural formula.



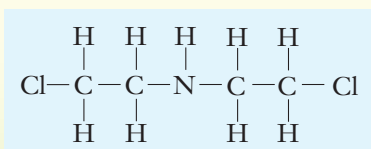
The model shows four carbon atoms (C), ten hydrogen atoms (H), and one oxygen atom (O), so the chemical formula is $\text{C}_4\text{H}_{10}\text{O}$.

- (b) This space-filling model shows that the atoms are bonded together as shown by the structural formula.



The model shows one carbon atom (C), two fluorine atoms (F), and two chlorine atoms (Cl), so the chemical formula is CF_2Cl_2 .

- (c) This ball-and-stick model shows that the atoms are bonded together as shown by the structural formula.

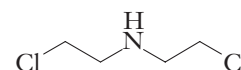
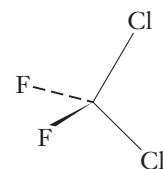
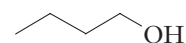


The model shows four carbon atoms (C), nine hydrogen atoms (H), one nitrogen atom (N), and two chlorine atoms (Cl), so the chemical formula is $\text{C}_4\text{H}_9\text{NCl}_2$.

► At this stage, you should not worry if you don't know the order in which the elements should appear in the chemical formula.

STOP & THINK

Chemists use a shorthand system for drawing the structures of organic compounds. Carbon and hydrogen atoms bonded to the carbon atoms are sometimes not drawn using their elemental symbols. Carbons are understood to be located at ends and corners of bond lines and have enough hydrogen atoms attached to give each carbon a total of four bonds. This is sometimes called *organic line notation*; examples of the three structures in Example 2-1 are shown below.



During your study of chemistry you will have many occasions to refer to compounds by name. In these early chapters, we will see how a few compounds should be named. More comprehensive rules for naming compounds are presented at the appropriate places later in the text.

Table 2-1 includes examples of names for a few common molecular compounds. You should learn that short list before proceeding much farther in this textbook. We will name many more molecular compounds as we encounter them in later chapters.

2-2 Ions and Ionic Compounds

► The words “cation” (kat’i-on) and “anion” (an’i-on) and their relationship to cathode and anode will be described in Chapter 21.

► The general term “formula unit” applies to molecular or ionic compounds, whereas the more specific term “molecule” applies only to elements and compounds that exist as discrete molecules.

► In this text, we use the standard convention of representing multiple charges with the number before the sign, e.g., Ca^{2+} , *not* Ca^{+2} and SO_4^{2-} , *not* SO_4^{-2} .

So far we have discussed only compounds that exist as discrete molecules. Some compounds, such as sodium chloride, NaCl , consist of collections of large numbers of ions. An **ion** is an atom or group of atoms that carries an electric charge. Ions that possess a *positive* charge, such as the sodium ion, Na^+ , are called **cations**. Those carrying a *negative* charge, such as the chloride ion, Cl^- , are called **anions**. The charge on an ion *must* be included as a superscript on the right side of the chemical symbol(s) when we write the formula for the individual ion.

As we will discuss in detail in Chapter 4, an atom consists of a very small, very dense, positively charged *nucleus* surrounded by a diffuse distribution of negatively charged particles called *electrons*. The number of positive charges in the nucleus defines the identity of the element to which the atom corresponds. Electrically neutral atoms contain the same number of electrons outside the nucleus as positive charges (protons) within the nucleus. Ions are formed when neutral atoms lose or gain electrons. An Na^+ ion is formed when a sodium atom loses one electron, and a Cl^- ion is formed when a chlorine atom gains one electron.

The compound NaCl consists of an extended array of Na^+ and Cl^- ions (Figure 2-2). Within the crystal (though not on the surface) each Na^+ ion is surrounded at equal distances by six Cl^- ions, and each Cl^- ion is similarly surrounded by six Na^+ ions. *Any* compound, whether ionic or molecular, is electrically neutral; that is, it has no net charge. In NaCl this means that the Na^+ and Cl^- ions are present in a 1:1 ratio, and this is indicated by the formula NaCl .

Because there are no “molecules” of ionic substances, we should not refer to “a molecule of sodium chloride, NaCl ,” for example. Instead, we refer to a **formula unit** of NaCl , which consists of one Na^+ ion and one Cl^- ion. Likewise, one formula unit of CaCl_2 consists of one Ca^{2+} ion and two Cl^- ions. We speak of the formula unit of all ionic compounds as the smallest, whole-number ratios of ions that yield neutral representations. It is also acceptable to refer to a formula unit of a molecular compound. One formula unit of propane, C_3H_8 , is the same as one molecule of C_3H_8 ; it contains three C atoms and eight H atoms bonded together into a group. For the present, we will tell you which substances are ionic and which are molecular when it is important to know. Later you will learn to make the distinction yourself.

Polyatomic ions are groups of atoms that bear an electric charge. The first atom in the formula is usually the central atom to which the other atoms are bonded to make a stable unit. Examples include the ammonium ion, NH_4^+ ; the sulfate ion, SO_4^{2-} ; and the

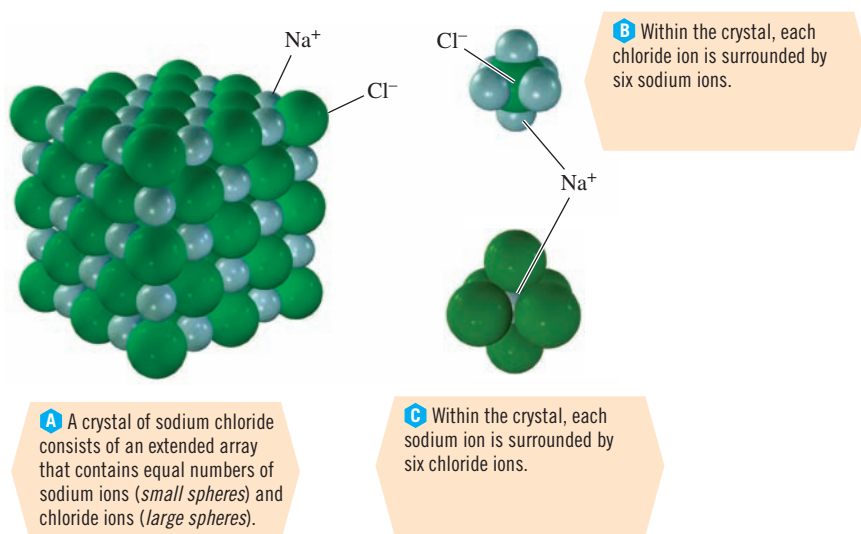


Figure 2-2 The arrangement of ions in NaCl .

Table 2-2 Formulas, Ionic Charges, and Names of Some Common Ions

Common Cations (positive ions)			Common Anions (negative ions)		
Formula	Charge	Name	Formula	Charge	Name
Li^+	1+	lithium	F^-	1-	fluoride
Na^+	1+	sodium	Cl^-	1-	chloride
K^+	1+	potassium	Br^-	1-	bromide
NH_4^+	1+	ammonium	I^-	1-	iodide
Ag^+	1+	silver	OH^-	1-	hydroxide
Mg^{2+}	2+	magnesium	CH_3COO^-	1-	acetate
Ca^{2+}	2+	calcium	NO_3^-	1-	nitrate
Zn^{2+}	2+	zinc	O^{2-}	2-	oxide
Cu^+	1+	copper(I)	S^{2-}	2-	sulfide
Cu^{2+}	2+	copper(II)	SO_4^{2-}	2-	sulfate
Fe^{2+}	2+	iron(II)	SO_3^{2-}	2-	sulfite
Fe^{3+}	3+	iron(III)	CO_3^{2-}	2-	carbonate
Al^{3+}	3+	aluminum	PO_4^{3-}	3-	phosphate

STOP & THINK

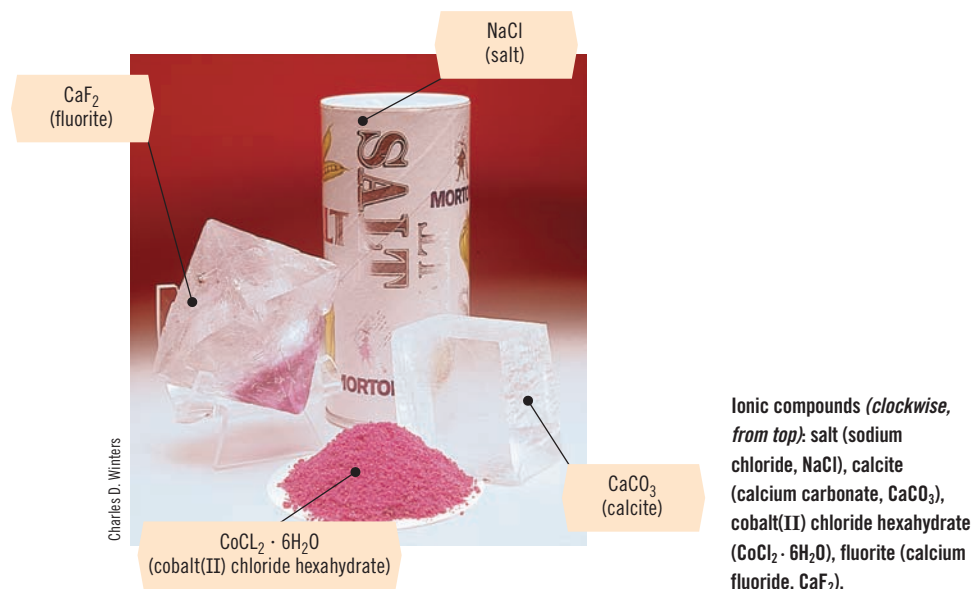
It is very important to learn the names, formulas, and charges of the common polyatomic ions listed in Table 2-2 and recognize them in chemical formulas.

► As we will see, some metals can form more than one kind of ion with a positive charge. For such metals, we specify which ion we mean with a Roman numeral, for example, iron(II) or iron(III). Because zinc forms no stable ions other than Zn^{2+} , we do not need to use Roman numerals in its name.

nitrate ion, NO_3^- . Table 2-2 shows the formulas, ionic charges, and names of some common ions. When writing the formula of a polyatomic compound, we show groups in parentheses when they appear more than once. For example, $(\text{NH}_4)_2\text{SO}_4$ represents a compound that has two NH_4^+ ions for each SO_4^{2-} ion.

2-3 Names and Formulas of Some Ionic Compounds

The names of some common ions appear in Table 2-2. You will need to know the names and formulas of these frequently encountered ions. They can be used to write the formulas and names of many ionic compounds. We write the formula of an ionic compound by adjusting the relative numbers of positive and negative ions so their total charges cancel (i.e., add to zero). The name of an ionic compound is formed by giving the names of the ions, with the positive ion named first.



Unless otherwise noted, all content on this page is © Cengage Learning.



Problem-Solving Tip Where to Start in Learning to Name Compounds

You may not be sure of the best point to start learning the naming of compounds. It has been found that before rules for naming can make much sense or before we can expand our knowledge to more complex compounds, we need to know the names and formulas in Tables 2-1 and 2-2. If you are unsure of your ability to recall a name or a formula in Tables 2-1 and 2-2 when given the other, prepare flash cards, lists, and so on that you can use to learn these tables.

EXAMPLE 2-2 Formulas for Ionic Compounds



Write the formulas for the following ionic compounds: (a) sodium fluoride, (b) calcium fluoride, (c) iron(II) sulfate, (d) zinc phosphate.

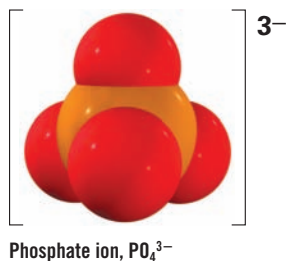
Plan

In each case, we identify the chemical formulas of the ions from Table 2-2. These ions must be present in the simplest whole-number ratio that gives the compound *no net charge*. Recall that the formulas and names of ionic compounds are written by giving the positively charged ion first.

Solution

- The formula for the sodium ion is Na^+ , and the formula for the fluoride ion is F^- (see Table 2-2). Because the charges on these two ions are equal in magnitude, the ions must be present in equal numbers, or in a 1:1 ratio. Thus, the formula for sodium fluoride is NaF .
- The formula for the calcium ion is Ca^{2+} and the formula for the fluoride ion is F^- . Now each positive ion (Ca^{2+}) provides twice as much charge as each negative ion (F^-). So there must be twice as many F^- ions as Ca^{2+} ions to equalize the charge. This means that the ratio of calcium to fluoride ions is 1:2. So the formula for calcium fluoride is CaF_2 .
- The iron(II) ion is Fe^{2+} , and the sulfate ion is SO_4^{2-} . As in part (a), the equal magnitudes of positive and negative charges tell us that the ions must be present in equal numbers, or in a 1:1 ratio. The formula for iron(II) sulfate is FeSO_4 .
- The zinc ion is Zn^{2+} , and the phosphate ion is PO_4^{3-} . Now it will take *three* Zn^{2+} ions to account for as much charge (6+ total) as would be present in *two* PO_4^{3-} ions (6- total). So the formula for zinc phosphate is $\text{Zn}_3(\text{PO}_4)_2$.

You should now work Exercises 16 and 23.



EXAMPLE 2-3 Names for Ionic Compounds



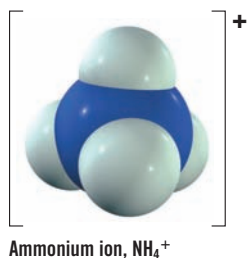
Name the following ionic compounds: (a) $(\text{NH}_4)_2\text{S}$, (b) $\text{Cu}(\text{NO}_3)_2$, (c) ZnCl_2 , (d) $\text{Fe}_2(\text{CO}_3)_3$.

Plan

In naming ionic compounds, it is helpful to inspect the formula for atoms or groups of atoms that we recognize as representing familiar ions.

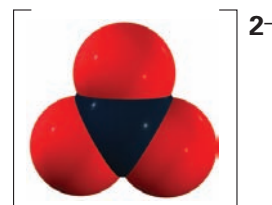
Solution

- The presence of the polyatomic grouping NH_4 in the formula suggests to us the presence of the ammonium ion, NH_4^+ . There are two of these, each accounting for 1+ in charge. To balance this, the single S must account for 2- in charge, or S^{2-} , which we recognize as the sulfide ion. Thus, the name of the compound is **ammonium sulfide**.



- (b) The NO_3 grouping in the formula tells us that the nitrate ion, NO_3^- , is present. Two of these nitrate ions account for $2 \times 1^- = 2^-$ in negative charge. To balance this, copper must account for 2^+ charge and be the copper(II) ion. The name of the compound is **copper(II) nitrate**.
- (c) The positive ion present is zinc ion, Zn^{2+} , and the negative ion is chloride, Cl^- . The name of the compound is **zinc chloride**.
- (d) Each CO_3 grouping in the formula must represent the carbonate ion, CO_3^{2-} . The presence of *three* such ions accounts for a total of 6^- in negative charge, so there must be a total of 6^+ present in positive charge to balance this. It takes two iron ions to provide this 6^+ , so each ion must have a charge of 3^+ and be Fe^{3+} , the iron(III) ion, or ferric ion. The name of the compound is **iron(III) carbonate**.

You should now work Exercises 15 and 22.



Carbonate ion, CO_3^{2-}

► We use the information that the carbonate ion has a 2^- charge to find the charge on the iron ions. The total charges must add up to zero.

A more extensive discussion on naming compounds appears in Chapter 6.

2-4 Atomic Weights

As the chemists of the eighteenth and nineteenth centuries painstakingly sought information about the compositions of compounds and tried to systematize their knowledge, it became apparent that each element has a characteristic mass relative to every other element. Although these early scientists did not have the experimental means to measure the mass of each kind of atom, they succeeded in defining a *relative* scale of atomic masses.

An early observation was that carbon and hydrogen have relative atomic masses, also traditionally called **atomic weights (AW)**, of approximately 12 and 1, respectively. Thousands of experiments on the compositions of compounds have resulted in the establishment of a scale of relative atomic weights based on the **atomic mass unit (amu)**, which is defined as *exactly $\frac{1}{12}$ of the mass of an atom of a particular kind of carbon atom, called carbon-12*.

On this scale, the atomic weight of hydrogen (H) is 1.00794 amu, that of sodium (Na) is 22.989768 amu, and that of magnesium (Mg) is 24.3050 amu. This tells us that Na atoms have nearly 23 times the mass of H atoms, and Mg atoms are about 24 times heavier than H atoms.

When you need values of atomic weights, consult the periodic table or the alphabetical listing of elements on the inside covers of this book.

► The term “atomic weight” is widely accepted because of its traditional use, although it is properly a mass rather than a weight. “Atomic mass” is often used and is technically more accurate. As you probably know, the weight of an object of a particular mass is the result of a gravitational attraction on the object. In chemistry, we are always comparing amounts of substances under the same gravitation, so any weight ratio is the same as the mass ratio.

2-5 The Mole

Even the smallest bit of matter that can be handled reliably contains an enormous number of atoms. So we must deal with large numbers of atoms in any real situation, and some unit for conveniently describing a large number of atoms is desirable. The idea of using a unit to describe a particular number (amount) of objects has been around for a long time. You are already familiar with the dozen (12 items) and the gross (144 items).

The SI unit for amount is the **mole**, abbreviated mol. It is *defined* as the amount of substance that contains as many entities (atoms, molecules, or other particles) as there are atoms in exactly 0.012 kg of pure carbon-12 atoms. Many experiments have refined the number, and the currently accepted value is

► “Mole” is derived from the Latin word *moles*, which means “a mass.” “Molecule” is the diminutive form of this word and means “a small mass.”

$$1 \text{ mole} = 6.02214179 \times 10^{23} \text{ particles}$$

This number, often rounded to 6.022×10^{23} , is called **Avogadro's number** in honor of Amedeo Avogadro (1776–1856), whose contributions to chemistry are discussed in Section 12-8.

According to its definition, the mole unit refers to a fixed number of items, the identities of which must be specified. Just as we speak of a dozen eggs or a pair of aces, we refer to a mole of atoms or a mole of molecules (or a mole of ions, electrons, or other particles). We could even think about a mole of eggs, although the size of the required carton staggers the imagination! Helium exists as discrete He atoms, so one mole of helium consists of 6.022×10^{23} He *atoms*. Hydrogen commonly exists as diatomic (two-atom) molecules, so one mole of hydrogen is 6.022×10^{23} H₂ *molecules* and $2(6.022 \times 10^{23})$ H atoms.

Every kind of atom, molecule, or ion has a definite characteristic mass. It follows that one mole of a given pure substance also has a definite mass, regardless of the source of the sample. This idea is of central importance in many calculations throughout the study of chemistry and the related sciences.

Because the mole is defined as the number of atoms in 0.012 kg (or 12 g) of carbon-12, and the atomic mass unit is defined as $\frac{1}{12}$ of the mass of a carbon-12 atom, the following convenient relationship is true:

The mass of one mole of *atoms* of a pure element in grams is numerically equal to the atomic weight of that element in atomic mass units. This is also called the **molar mass** of the element; its units are grams/mole, also written as g/mol or $\text{g} \cdot \text{mol}^{-1}$.

For instance, if you obtain a pure sample of the metallic element titanium (Ti), whose atomic weight is 47.88 amu, and measure out 47.88 g of it, you will have one mole, or 6.022×10^{23} titanium atoms.

► The atomic weight of iron (Fe) is 55.847 amu. Assume that one dozen large eggs weighs 24 oz.

The symbol for an element is used in several ways: (1) to identify the element, (2) to represent one atom of the element, or (3) to represent one mole of atoms of the element. The last interpretation will be extremely useful in calculations in Chapter 3.

A quantity of a substance may be expressed in a variety of ways. For example, consider a dozen eggs and 55.847 grams (or one mole) of iron (Figure 2-3). We can express the amount of eggs or iron present in any of several units. We can then construct unit factors to relate an amount of the substance expressed in one kind of unit to the same amount expressed in another unit.

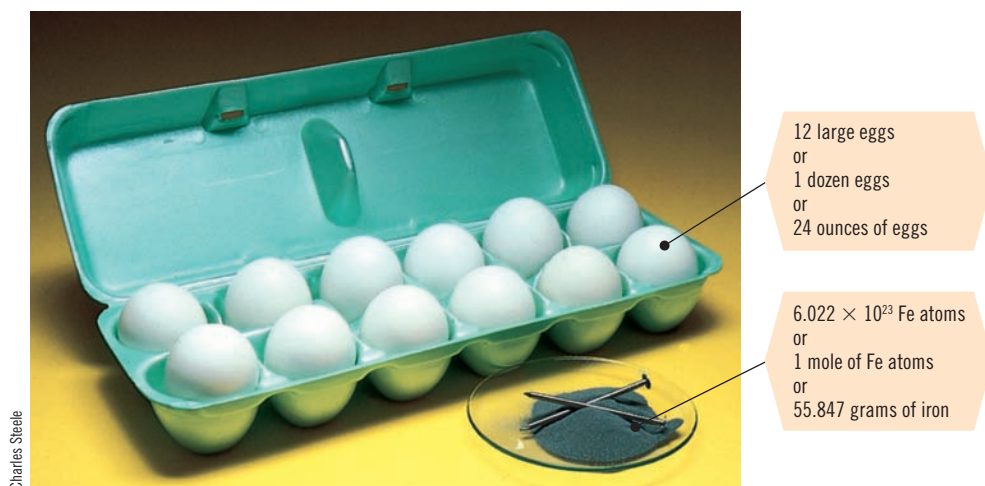


Figure 2-3 Three ways of representing amounts.

Unless otherwise noted, all content on this page is © Cengage Learning.

Unit Factors for Eggs	Unit Factors for Iron
12 eggs	6.022×10^{23} Fe atoms
1 doz eggs	1 mol Fe atoms
12 eggs	6.022×10^{23} Fe atoms
24 oz eggs	55.847 g Fe
and so on	and so on

As Table 2-3 suggests, the concept of a mole as applied to atoms is especially useful. It provides a convenient basis for comparing the masses of equal numbers of atoms of different elements.

Figure 2-4 shows what one mole of atoms of each of some common elements looks like. Each of the examples in Figure 2-4 represents 6.022×10^{23} atoms of the element.

The relationship between the mass of a sample of an element and the number of moles of atoms in the sample is illustrated in Example 2-4.

Table 2-3 Mass of One Mole of Atoms of Some Common Elements

Element	Atomic Weight	A Sample with a Mass of	Contains
carbon	12.0	12.0 g C	6.02×10^{23} C atoms or 1 mol of C atoms
titanium	47.9	47.9 g Ti	6.02×10^{23} Ti atoms or 1 mol of Ti atoms
bromine	79.9	79.9 g Br ₂	6.02×10^{23} Br atoms or 1 mol of Br atoms (3.01×10^{23} Br ₂ molecules or $\frac{1}{2}$ mole of Br ₂ molecules)
hydrogen	1.0	1.0 g H ₂	6.02×10^{23} H atoms or 1 mol of H atoms (3.01×10^{23} H ₂ molecules or $\frac{1}{2}$ mol of H ₂ molecules)
sulfur	32.1	32.1 g S ₈	6.02×10^{23} S atoms or 1 mol of S atoms (0.753×10^{23} S ₈ molecules or $\frac{1}{8}$ mol of S ₈ molecules)



Figure 2-4 One mole of atoms of some common elements.

Unless otherwise noted, all content on this page is © Cengage Learning.

In this textbook we usually work problems involving atomic weights (masses) or formula weights (masses) rounded to only one decimal place. We round the answer further if initial data do not support the number of significant figures obtained using the rounded atomic weights. Similarly, if the initial data indicate that more significant figures are justified, we will work such problems using atomic weights and formula weights containing values beyond the tenths place.

EXAMPLE 2-4 Moles of Atoms

How many moles of atoms does 136.9 g of iron metal contain?

Plan

The atomic weight of iron is 55.85 amu. This tells us that the molar mass of iron is 55.85 g/mol, or that one mole of iron atoms is 55.85 g of iron. We can express this as either of two unit factors:

$$\frac{1 \text{ mol Fe atoms}}{55.85 \text{ g Fe}} \quad \text{or} \quad \frac{55.85 \text{ g Fe}}{1 \text{ mol Fe atoms}}$$

Because one mole of iron has a mass of 55.85 g, we expect that 136.9 g will be a fairly small number of moles (greater than 1, but less than 10).

Solution

$$\underline{\hspace{1cm}} \text{ mol Fe atoms} = 136.9 \text{ g Fe} \times \frac{1 \text{ mol Fe atoms}}{55.85 \text{ g Fe}} = 2.451 \text{ mol Fe atoms}$$

You should now work Exercises 32 and 40.

Once the number of moles of atoms of an element is known, the number of atoms in the sample can be calculated, as Example 2-5 illustrates.

EXAMPLE 2-5 Numbers of Atoms

How many atoms are contained in 2.451 mol of iron?

Plan

One mole of atoms of an element contains Avogadro's number of atoms, or 6.022×10^{23} atoms. This lets us generate the two unit factors

$$\frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol atoms}} \quad \text{and} \quad \frac{1 \text{ mol atoms}}{6.022 \times 10^{23} \text{ atoms}}$$

Solution

$$\underline{\hspace{1cm}} \text{ Fe atoms} = 2.451 \text{ mol Fe atoms} \times \frac{6.022 \times 10^{23} \text{ Fe atoms}}{1 \text{ mol Fe atoms}} = 1.476 \times 10^{24} \text{ Fe atoms}$$

We expected the number of atoms in more than two moles of atoms to be a very large number. Written in nonscientific notation, the answer to this example is: 1,476,000,000,000,000,000,000.

You should now work Exercise 42.

If we know the atomic weight of an element on the carbon-12 scale, we can use the mole concept and Avogadro's number to calculate the *average* mass of one atom of that element in grams (or any other mass unit we choose).

► To the required four significant figures, 1 mol Fe atoms = 55.85 g Fe.

STOP & THINK

When you are given the mass (or weight) of any substance in grams (or any other mass or weight unit) you almost always need to convert it into moles to do chemical calculations. Formula weight is always greater than 1 (except for H atoms), so the number of moles in a sample is always a smaller number than the mass in grams.

STOP & THINK

Try to name this number with its many zeroes. One mole of anything contains a huge number of atoms or molecules (Avogadro's number). Thus the number of atoms or molecules is always *much* larger than the number of moles or the mass in grams. Be sure to carry units through every calculation.



CHEMISTRY IN USE

Avogadro's Number

If you think that the value of Avogadro's number, 6×10^{23} , is too large to be useful to anyone but chemists, look up into the sky on a clear night. You may be able to see about 3000 stars with the naked eye, but the total number of stars swirling around you in the known universe is approximately equal to Avogadro's number. Just think, the known universe contains approximately one mole of stars! You don't have to leave Earth to encounter such large numbers. The water in the Pacific Ocean has a volume of about 6×10^{23} mL and a mass of about 6×10^{23} g.

Avogadro's number is almost incomprehensibly large. For example, if one mole of dollars had been given away at the rate of a million dollars per second beginning when the earth first formed some 4.5 billion years ago, would any remain today? Surprisingly, about three-fourths of the original mole of dollars would be left today; it would take about 14,500,000,000 more years to give away the remaining money at \$1 million per second.

Computers can be used to provide another illustration of the magnitude of Avogadro's number. If a computer can count up to one billion in one second, it would take that computer about 20 million years to count up to 6×10^{23} . In contrast, recorded human history goes back only a few thousand years.

The impressively large size of Avogadro's number can give us very important insights into the very small sizes of individual molecules. Suppose one drop of water evaporates in

one hour. There are about 20 drops in one milliliter of water, which weighs one gram. So one drop of water is about 0.05 g of water. How many H_2O molecules evaporate per second?

$$\begin{aligned} \frac{\text{H}_2\text{O molecules}}{1 \text{ s}} &= \frac{0.05 \text{ g H}_2\text{O}}{1 \text{ h}} \times \frac{1 \text{ mol H}_2\text{O}}{18 \text{ g H}_2\text{O}} \times \\ &\quad \frac{6 \times 10^{23} \text{ H}_2\text{O molecules}}{1 \text{ mol H}_2\text{O}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} \\ &= 5 \times 10^{17} \text{ H}_2\text{O molecules/s} \end{aligned}$$

5×10^{17} H_2O molecules evaporating per second is five hundred million billion H_2O molecules evaporating per second—a number that is beyond our comprehension! This calculation helps us to recognize that water molecules are incredibly small. There are approximately 1.7×10^{21} water molecules in a single drop of water.

By gaining some appreciation of the vastness of Avogadro's number, we gain a greater appreciation of the extremely tiny volumes occupied by individual atoms, molecules, and ions.

RONALD DELORENZO

MIDDLE GEORGIA COLLEGE

ORIGINAL CONCEPT BY LARRY NORDELL

EXAMPLE 2-6 Masses of Atoms

Calculate the average mass of one iron atom in grams.

Plan

We expect that the mass of a single atom in grams would be a *very* small number. We know that one mole of Fe atoms has a mass of 55.85 g and contains 6.022×10^{23} Fe atoms. We use this information to generate unit factors to carry out the desired conversion.

Solution

$$\frac{? \text{ g Fe}}{\text{Fe atom}} = \frac{55.85 \text{ g Fe}}{1 \text{ mol Fe atoms}} \times \frac{1 \text{ mol Fe atoms}}{6.022 \times 10^{23} \text{ Fe atoms}} = 9.274 \times 10^{-23} \text{ g Fe/Fe atom}$$

Thus, we see that the average mass of one Fe atom is only 9.274×10^{-23} g, that is, 0.00000000000000000000009274 g.

Example 2-6 demonstrates how small atoms are and why it is necessary to use large numbers of atoms in practical work. Example 2-7 will help you to appreciate the huge magnitude of Avogadro's number.

STOP & THINK

For any substance, the amount that we can manipulate or measure contains a huge number of atoms or molecules, so the mass of any atom or molecule must be a tiny fraction of a gram.

EXAMPLE 2-7 Avogadro's Number

A stack of 500 sheets of typing paper is 1.9 inches thick. Calculate the thickness, in inches and in miles, of a stack of typing paper that contains one mole (Avogadro's number) of sheets.

Plan

We construct unit factors from the data given, from conversion factors in Table 1-8, and from Avogadro's number.

Solution

$$\underline{?} \text{ in.} = 1 \text{ mol sheets} \times \frac{6.022 \times 10^{23} \text{ sheets}}{1 \text{ mol sheets}} \times \frac{1.9 \text{ in.}}{500 \text{ sheets}} = 2.3 \times 10^{21} \text{ in.}$$

$$\underline{?} \text{ mi} = 2.3 \times 10^{21} \text{ in.} \times \frac{1 \text{ ft}}{12 \text{ in.}} \times \frac{1 \text{ mi}}{5280 \text{ ft}} = 3.6 \times 10^{16} \text{ mi.}$$

By comparison, the sun is about 93 million miles from the earth. This stack of paper would make 390 million stacks that reach from the earth to the sun.

► Imagine the number of trees required to make this much paper! This would weigh about 5×10^{20} kg, which far exceeds the total mass of all the trees on earth. The mass of the earth is about 6×10^{24} kg.

Problem-Solving Tip When Do We Round?

Even though the number 1.9 has two significant figures, we carry the other numbers in Example 2-7 to more significant figures. Then we round at the end to the appropriate number of significant figures. The numbers in the distance conversions are exact numbers.

2-6 Formula Weights, Molecular Weights, and Moles

► Formula weight is more accurately called formula mass.

The **formula weight (FW)** of a substance is the sum of the atomic weights (AW) of the elements in the formula, each taken the number of times the element occurs. Hence a formula weight gives the mass of one formula unit in atomic mass units.

Formula weights, like the atomic weights on which they are based, are relative masses. The formula weight for sodium hydroxide, NaOH (rounded off to the nearest 0.1 amu), is found as follows.

Number of Atoms of Stated Kind	× Mass of One Atom	= Mass Due to Element
$1 \times \text{Na} = 1$	× 23.0 amu	= 23.0 amu of Na
$1 \times \text{H} = 1$	× 1.0 amu	= 1.0 amu of H
$1 \times \text{O} = 1$	× 16.0 amu	= 16.0 amu of O

$$\text{Formula weight of NaOH} = 40.0 \text{ amu}$$

The term “formula weight” is correctly used for either ionic or molecular substances. When we refer specifically to molecular (non-ionic) substances, that is, substances that exist as discrete molecules, we often use the term **molecular weight (MW)**.

EXAMPLE 2-8 Formula Weights

Calculate the formula weight (molecular weight) of acetic acid (the active ingredient in vinegar), CH_3COOH , using rounded values for atomic weights given in the International Table of Atomic Weights inside the front cover of the text.

Plan

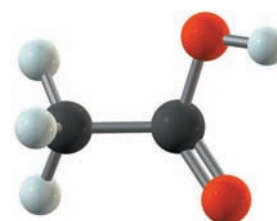
We add the atomic weights of the elements in the formula, each multiplied by the number of times the element occurs.

Solution

Number of Atoms of Stated Kind	$\times$ Mass of One Atom	= Mass Due to Element
$2 \times \text{C} = 2$	$\times 12.0 \text{ amu}$	= 24.0 amu of C
$4 \times \text{H} = 4$	$\times 1.0 \text{ amu}$	= 4.0 amu of H
$2 \times \text{O} = 2$	$\times 16.0 \text{ amu}$	= 32.0 amu of O

Formula weight (molecular weight) of acetic acid = 60.0 amu

You should now work Exercise 28.



A Ball-and-stick model, CH_3COOH



B Space-filling model of an acetic acid molecule, CH_3COOH

The amount of substance that contains the mass in grams numerically equal to its formula weight in amu contains 6.022×10^{23} formula units, or one *mole* of the substance. This is sometimes called the *molar mass* of the substance. Molar mass is *numerically equal* to the formula weight of the substance (the atomic weight for atoms of elements) and has the units grams/mole (g/mol).

One mole of sodium hydroxide is 40.0 g of NaOH , and one mole of acetic acid is 60.0 g of CH_3COOH . One mole of any molecular substance contains 6.02×10^{23} molecules of that substance, as Table 2-4 illustrates.

Because no simple NaCl molecules exist at ordinary temperatures, it is inappropriate to refer to the “molecular weight” of NaCl or any ionic compound. One mole of an ionic compound contains 6.02×10^{23} *formula units* of the substance. Recall that one formula unit of sodium chloride consists of one sodium ion, Na^+ and one chloride ion, Cl^- . One mole, or 58.4 g, of NaCl contains 6.02×10^{23} Na^+ ions and 6.02×10^{23} ions (Table 2-5).

STOP & THINK

The formula weight is the sum of atomic weights. The smallest atomic weight (H) is 1.0, so all other formula weights must be greater than 1 amu.

Table 2-4 One Mole of Some Common Molecular Substances

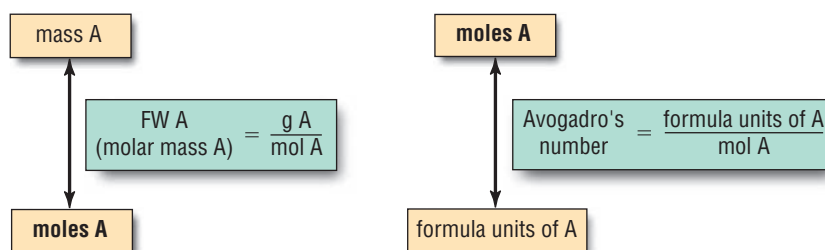
Substance	Molecular Weight	A Sample with a Mass of	Contains
oxygen	32.0 g/mol	32.0 g O_2	1 mol of O_2 molecules or 6.02×10^{23} molecules O_2 ($2 \times 6.02 \times 10^{23}$ atoms of O)
water	18.0 g/mol	18.0 g H_2O	1 mol of H_2O molecules or 6.02×10^{23} molecules of H_2O ($2 \times 6.02 \times 10^{23}$ atoms of H and 6.02×10^{23} atoms of O)
methane	16.0 g/mol	16.0 g CH_4	1 mol of CH_4 molecules or 6.02×10^{23} molecules of CH_4 ($4 \times 6.02 \times 10^{23}$ atoms of H and 6.02×10^{23} atoms of C)
sucrose (sugar)	342.3 g/mol	342.3 g $\text{C}_{12}\text{H}_{22}\text{O}_{11}$	1 mol of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ molecules or 6.02×10^{23} molecules of sucrose ($12 \times 6.02 \times 10^{23}$ atoms of C, $22 \times 6.02 \times 10^{23}$ atoms of H, and $11 \times 6.02 \times 10^{23}$ atoms of O)

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 2-5 One Mole of Some Ionic Compounds

Compound	Formula Weight	A Sample with a Mass of 1 Mol	Contains
sodium chloride	58.4 g/mol	58.4 g NaCl	$(6.02 \times 10^{23} \text{ Na}^+ \text{ ions or } 1 \text{ mol of Na}^+ \text{ ions})$ and $(6.02 \times 10^{23} \text{ Cl}^- \text{ ions or } 1 \text{ mol of Cl}^- \text{ ions})$
calcium chloride	111.0 g/mol	111.0 g CaCl ₂	$(6.02 \times 10^{23} \text{ Ca}^{2+} \text{ ions or } 1 \text{ mol of Ca}^{2+} \text{ ions})$ and $(2 \times 6.02 \times 10^{23} \text{ Cl}^- \text{ ions or } 2 \text{ mol of Cl}^- \text{ ions})$
aluminum sulfate	342.1 g/mol	342.1 g Al ₂ (SO ₄) ₃	$(2 \times 6.02 \times 10^{23} \text{ Al}^{3+} \text{ ions or } 2 \text{ mol of Al}^{3+} \text{ ions})$ and $(3 \times 6.02 \times 10^{23} \text{ SO}_4^{2-} \text{ ions or } 3 \text{ mol of SO}_4^{2-} \text{ ions})$

The mole concept, together with Avogadro's number, provides important connections among the extensive properties mass of substance, number of moles of substance, and number of molecules or ions. These are summarized as follows:



The following examples show the relations between numbers of molecules, atoms, or formula units and their masses.

EXAMPLE 2-9 Masses of Molecules

What is the mass in grams of 10.0 million SO₂ molecules?

Plan

One mole of SO₂ contains 6.02×10^{23} SO₂ molecules and has a mass of 64.1 grams.

Solution

$$\begin{aligned} \text{? g SO}_2 &= 10.0 \times 10^6 \text{ SO}_2 \text{ molecules} \times \frac{64.1 \text{ g SO}_2}{6.02 \times 10^{23} \text{ SO}_2 \text{ molecules}} \\ &= 1.06 \times 10^{-15} \text{ g SO}_2 \end{aligned}$$

Ten million SO₂ molecules have a mass of only 0.00000000000000106 g. Commonly used analytical balances are capable of weighing to ± 0.0001 g.

You should now work Exercise 44.

STOP & THINK

When fewer than four significant figures are needed in calculations, Avogadro's number may be rounded to 6.02×10^{23} . The mass of any molecule is a very tiny number of grams.

EXAMPLE 2-10 Moles

How many (a) moles of O_2 , (b) O_2 molecules, and (c) O atoms are contained in 40.0 g of oxygen gas (dioxygen) at 25°C?

Plan

We construct the needed unit factors from the following equalities: (a) the mass of one mole of O_2 is 32.0 g (molar mass $O_2 = 32.0 \text{ g/mol}$); (b) one mole of O_2 contains 6.02×10^{23} O_2 molecules; (c) one O_2 molecule contains two O atoms.

Solution

One mole of O_2 contains 6.02×10^{23} O_2 molecules, and its mass is 32.0 g.

$$(a) \text{ } \underline{\hspace{1cm}} \text{ mol } O_2 = 40.0 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.0 \text{ g } O_2} = 1.25 \text{ mol } O_2$$

$$(b) \text{ } \underline{\hspace{1cm}} \text{ } O_2 \text{ molecules} = 40.0 \text{ g } O_2 \times \frac{6.02 \times 10^{23} \text{ } O_2 \text{ molecules}}{32.0 \text{ g } O_2} \\ = 7.52 \times 10^{23} \text{ molecules}$$

Or, we can use the number of moles of O_2 calculated in part (a) to find the number of O_2 molecules.

$$\underline{\hspace{1cm}} \text{ } O_2 \text{ molecules} = 1.25 \text{ mol } O_2 \times \frac{6.02 \times 10^{23} \text{ } O_2 \text{ molecules}}{1 \text{ mol } O_2} = 7.52 \times 10^{23} \text{ } O_2 \text{ molecules}$$

$$(c) \text{ } \underline{\hspace{1cm}} \text{ O atoms} = 40.0 \text{ g } O_2 \times \frac{6.02 \times 10^{23} \text{ } O_2 \text{ molecules}}{32.0 \text{ g } O_2} \times \frac{2 \text{ O atoms}}{1 \text{ } O_2 \text{ molecule}} \\ = 1.50 \times 10^{24} \text{ O atoms}$$

You should now work Exercise 36.

STOP & THINK

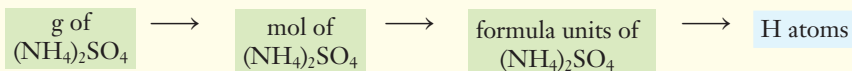
Use unit factors to help you with all conversions. (a) Number of moles is always less than the mass in grams. (b, c) Number of molecules and number of atoms is always *much* greater than the number of moles present.

EXAMPLE 2-11 Numbers of Atoms

Calculate the number of hydrogen atoms in 39.6 g of ammonium sulfate, $(NH_4)_2SO_4$.

Plan

One mole of $(NH_4)_2SO_4$ is 6.02×10^{23} formula units and has a mass of 132.1 g.

**Solution**

$$\underline{\hspace{1cm}} \text{ H atoms} = 39.6 \text{ g } (NH_4)_2SO_4 \times \frac{1 \text{ mol } (NH_4)_2SO_4}{132.1 \text{ g } (NH_4)_2SO_4} \times \frac{6.02 \times 10^{23} \text{ formula units } (NH_4)_2SO_4}{1 \text{ mol } (NH_4)_2SO_4} \times \frac{8 \text{ H atoms}}{1 \text{ formula units } (NH_4)_2SO_4} \\ = 1.44 \times 10^{24} \text{ H atoms}$$

You should now work Exercise 34.

► In Example 2-11, we relate (a) grams to moles, (b) moles to formula units, and (c) formula units to H atoms.

STOP & THINK

Remember to include both "types" of subscripts in figuring out the number of atoms! It is pretty easy to remember that the 4-subscript in $(NH_4)_2$ means that there are four H atoms. But don't forget to include the 2-subscript, which means that there are two NH_4 units present for a total of 8 H atoms.

2-7 Percent Composition and Formulas of Compounds

- AW = atomic weight (mass)
MW = molecular weight (mass)

As a check, we see that the percentages add to 100%.

If the formula of a compound is known, its chemical composition can be expressed as the mass percent of each element in the compound (percent composition). For example, one carbon dioxide molecule, CO_2 , contains one C atom and two O atoms. Percentage is the part divided by the whole times 100% (or simply parts per hundred), so we can represent the percent composition of carbon dioxide as follows:

$$\begin{aligned}\% \text{C} &= \frac{\text{mass of C}}{\text{mass of CO}_2} \times 100\% = \frac{\text{AW of C}}{\text{MW of CO}_2} \times 100\% = \frac{12.0 \text{ amu}}{44.0 \text{ amu}} \times 100\% = 27.3\% \text{ C} \\ \% \text{O} &= \frac{\text{mass of O}}{\text{mass of CO}_2} \times 100\% = \frac{2 \times \text{AW of O}}{\text{MW of CO}_2} \times 100\% = \frac{2(16.0 \text{ amu})}{44.0 \text{ amu}} \times 100\% = 72.7\% \text{ O}\end{aligned}$$

One *mole* of CO_2 (44.0 g) contains one *mole* of C atoms (12.0 g) and two *moles* of O atoms (32.0 g). We could therefore have used these masses in the preceding calculation. These numbers are the same as the ones used—only the units are different. In Example 2-12 we will base our calculation on one *mole* rather than one *molecule*.

EXAMPLE 2-12 Percent Composition

Calculate the percent composition by mass of HNO_3 .

Plan

We first calculate the mass of one mole as in Example 2-8. Then we express the mass of each element as a percent of the total.

Solution

The molar mass of HNO_3 is calculated first.

Number of Mol of Atoms	× Mass of One Mol of Atoms	= Mass Due to Element
$1 \times \text{H} = 1$	× 1.0 g	= 1.0 g of H
$1 \times \text{N} = 1$	× 14.0 g	= 14.0 g of N
$3 \times \text{O} = 3$	× 16.0 g	= 48.0 g of O

$$\text{Mass of 1 mol of HNO}_3 = 63.0 \text{ g}$$

Now, its percent composition is

$$\% \text{H} = \frac{\text{mass of H}}{\text{mass of HNO}_3} \times 100\% = \frac{1.0 \text{ g}}{63.0 \text{ g}} \times 100\% = 1.6\% \text{ H}$$

$$\% \text{N} = \frac{\text{mass of N}}{\text{mass of HNO}_3} \times 100\% = \frac{14.0 \text{ g}}{63.0 \text{ g}} \times 100\% = 22.2\% \text{ N}$$

$$\% \text{O} = \frac{\text{mass of O}}{\text{mass of HNO}_3} \times 100\% = \frac{48.0 \text{ g}}{63.0 \text{ g}} \times 100\% = 76.2\% \text{ O}$$

$$\text{Total} = 100.0\%$$

You should now work Exercise 62.

Nitric acid is 1.6% H, 22.2% N, and 76.2% O by mass. All samples of pure HNO_3 have this composition, according to the Law of Definite Proportions.

- When chemists use the % notation, they mean percent by mass unless they specify otherwise.

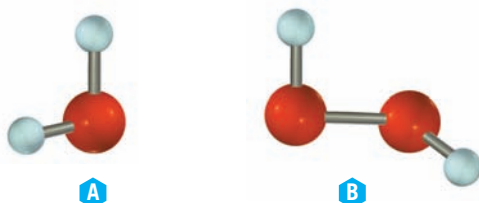


Problem-Solving Tip The Whole Is Equal to the Sum of Its Parts

Percentages must add to 100%. Roundoff errors may not cancel, however, and totals such as 99.9% or 100.1% may be obtained in calculations. As an alternative method of calculation, if we know all of the percentages except one, we can subtract their sum from 100% to obtain the remaining value.

2-8 Derivation of Formulas from Elemental Composition

The **simplest**, or **empirical**, **formula** for a compound is the smallest whole-number ratio of atoms present. For molecular compounds the **molecular formula** indicates the *actual* numbers of atoms present in a molecule of the compound. It may be the same as the simplest formula or else some whole-number multiple of it. For example, the simplest and molecular formulas for water are both H_2O ; however, for hydrogen peroxide, the empirical formula is HO , and the molecular formula is H_2O_2 .



A ball-and-stick model of (a) a molecule of water, H_2O , and (b) a molecule of hydrogen peroxide, H_2O_2

Each year thousands of new compounds are made in laboratories or discovered in nature. One of the first steps in characterizing a new compound is the determination of its percent composition. A *qualitative* analysis is performed to determine which elements are present in the compound. Then a *quantitative* analysis is performed to determine the *amount* of each element. Once the percent composition of a compound (or its elemental composition by mass) is known, the simplest formula can be determined.

EXAMPLE 2-13 Simplest Formulas

Compounds containing sulfur and oxygen are serious air pollutants; they represent the major cause of acid rain. Analysis of a sample of a pure compound reveals that it contains 50.1% sulfur and 49.9% oxygen by mass. What is the simplest formula of the compound?

Plan

One mole of atoms of any element is 6.02×10^{23} atoms, so the ratio of moles of atoms in any sample of a compound is the same as the ratio of atoms in that compound. This calculation is carried out in two steps.

Step 1: Let's consider 100.0 g of compound, which contains 50.1 g of S and 49.9 g of O. We calculate the number of moles of atoms of each.

Step 2: We then obtain a whole-number ratio between these numbers that gives the ratio of atoms in the sample and hence in the simplest formula for the compound.

Solution

$$\text{Step 1: } \underline{\hspace{1cm}} \text{ mol S atoms} = 50.1 \text{ g S} \times \frac{1 \text{ mol S atoms}}{32.1 \text{ g S}} = 1.56 \text{ mol S atoms}$$

$$\underline{\hspace{1cm}} \text{ mol O atoms} = 49.9 \text{ g O} \times \frac{1 \text{ mol O atoms}}{16.0 \text{ g O}} = 3.12 \text{ mol O atoms}$$

► Remember that *percent* means "parts per hundred."

► A simple and useful way to obtain whole-number ratios among several numbers follows: (a) Divide each number by the smallest number, and then, (b) if necessary, multiply all the resulting numbers by the smallest whole number that will eliminate fractions

Step 2: Now we know that 100.0 g of the compound contains 1.56 mol of S atoms and 3.12 mol of O atoms. We obtain a whole-number ratio between these numbers that gives the ratio of atoms in the simplest formula.

$$\frac{1.56}{1.56} = 1.00 \text{ S}$$

$$\frac{3.12}{1.56} = 2.00 \text{ O}$$

SO₂

You should now work Exercise 54.

The solution for Example 2-13 can be set up in tabular form.

► The “Relative Mass of Element” column is proportional to the mass of each element in grams. With this interpretation, the next column could be headed “Relative Number of *Moles* of Atoms.” Then the last column would represent the smallest whole-number ratios of *moles* of atoms. But because a mole is always the same number of items (atoms), that ratio is the same as the smallest whole-number ratio of atoms.

Element	Relative Mass of Element	Relative Number of Atoms (divide mass by AW)	Divide by Smallest Number	Smallest Whole-Number Ratio of Atoms
S	50.1	$\frac{50.1}{32.1} = 1.56$	$\frac{1.56}{1.56} = 1.00 \text{ S}$	SO₂
O	49.9	$\frac{49.9}{16.0} = 3.12$	$\frac{3.12}{1.56} = 2.00 \text{ O}$	

This tabular format provides a convenient way to solve simplest-formula problems, as the next example illustrates.

EXAMPLE 2-14 Simplest Formula

A 20.882-g sample of an ionic compound is found to contain 6.072 g of Na, 8.474 g of S, and 6.336 g of O. What is its simplest formula?

Plan

We reason as in Example 2-13, calculating the number of moles of each element and the ratio among them. Here we use the tabular format that was introduced earlier.

Solution

Element	Relative Mass of Element	Relative Number of Atoms (divide mass by AW)	Divide by Smallest Number	Convert Fractions to Whole Numbers (multiply by integer)	Smallest Whole-Number Ratio of Atoms
Na	6.072	$\frac{6.072}{23.0} = 0.264$	$\frac{0.264}{0.264} = 1.00$	$1.00 \times 2 = 2 \text{ Na}$	Na₂S₂O₃
S	8.474	$\frac{8.474}{32.1} = 0.264$	$\frac{0.264}{0.264} = 1.00$	$1.00 \times 2 = 2 \text{ S}$	
O	6.336	$\frac{6.336}{16.0} = 0.396$	$\frac{0.396}{0.264} = 1.50$	$1.50 \times 2 = 3 \text{ O}$	

The ratio of atoms in the simplest formula *must be a whole-number ratio* (by definition). To convert the ratio 1:1:1.5 to a whole-number ratio, each number in the ratio was multiplied by 2, which gave the simplest formula **Na₂S₂O₃**.

You should now work Exercise 56.

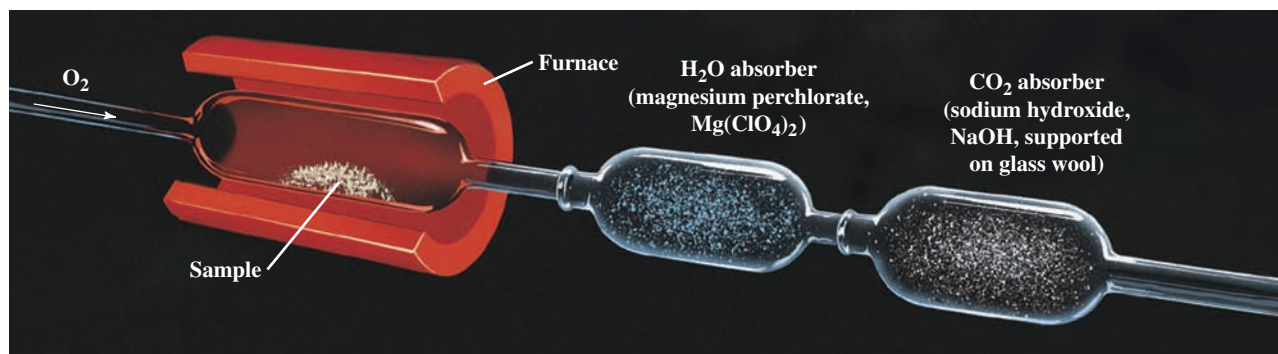


Figure 2-5 A combustion train used for carbon–hydrogen analysis. The increase in weight of the H_2O absorber can be converted into the amount of hydrogen present, while the increase in weight of the CO_2 absorber can be used to calculate the amount of carbon present.

Problem-Solving Tip Know Common Fractions in Decimal Form

As Example 2-14 illustrates, sometimes we must convert a fraction to a whole number by multiplying the fraction by the correct integer. But we must first recognize which fraction is represented by a nonzero part of a number. The decimal equivalents of the following fractions may be useful.

Decimal Equivalent (to two places)	Fraction	To convert to integer, multiply by
0.50	$\frac{1}{2}$	2
0.33	$\frac{1}{3}$	3
0.67	$\frac{2}{3}$	3
0.25	$\frac{1}{4}$	4
0.75	$\frac{3}{4}$	4
0.20	$\frac{1}{5}$	5

The fractions $\frac{2}{5}$, $\frac{3}{5}$, and $\frac{4}{5}$ are equal to 0.40, 0.60, and 0.80, respectively; these should be multiplied by 5.

When we use the procedure given in this section, we often obtain numbers such as 0.99 and 1.52. Because the results obtained by analysis of samples usually contain some error (as well as roundoff errors), we would interpret 0.99 as 1.0 and 1.52 as 1.5.

STOP & THINK
A simplest (empirical) formula must have only integer subscripts with no common factors.

STOP & THINK
Don't forget to multiply *all* calculated coefficients by this common factor to obtain the final integer coefficients!

Millions of compounds are composed of carbon, hydrogen, and oxygen. Analyses for C and H can be performed in a C–H combustion system (Figure 2-5). An accurately known mass of a compound is burned in a furnace in a stream of oxygen. This technique is often termed *combustion analysis*. The carbon and hydrogen in the sample are converted to carbon dioxide and water vapor, respectively. The resulting increases in masses of the CO_2 and H_2O absorbers can then be related to the masses and percentages of carbon and hydrogen in the original sample.

EXAMPLE 2-15 Percent Composition

Hydrocarbons are organic compounds composed entirely of hydrogen and carbon. A 0.1647-g sample of a pure hydrocarbon was burned in a C–H combustion train to produce 0.4931 g of CO_2 and 0.2691 g of H_2O . Determine the masses of C and H in the sample and the percentages of these elements in this hydrocarbon.

► Hydrocarbons are obtained from coal and coal tar and from oil and gas wells. The main use of hydrocarbons is as fuels. The simplest hydrocarbons are

methane	CH_4
ethane	C_2H_6
propane	C_3H_8
butane	C_4H_{10}

Plan

Step 1: We use the observed mass of CO_2 , 0.4931 g, to determine the mass of carbon in the original sample. There is one mole of carbon atoms, 12.01 g, in each mole of CO_2 , 44.01 g; we use this information to construct the unit factor

$$\frac{12.01 \text{ g C}}{44.01 \text{ g CO}_2}$$

Step 2: Likewise, we can use the observed mass of H_2O , 0.2691 g, to calculate the amount of hydrogen in the original sample. We use the fact that there are two moles of hydrogen atoms, 2.016 g, in each mole of H_2O , 18.02 g, to construct the unit factor

$$\frac{2.016 \text{ g H}}{18.02 \text{ g H}_2\text{O}}$$

Step 3: Then we calculate the percentages by mass of each element in turn, using the relationship

$$\% \text{element} = \frac{\text{g element}}{\text{g sample}} \times 100\%$$

Solution

$$\text{Step 1: } \text{? g C} = 0.4931 \text{ g CO}_2 \times \frac{12.01 \text{ g C}}{44.01 \text{ g CO}_2} = 0.1346 \text{ g C}$$

$$\text{Step 2: } \text{? g H} = 0.2691 \text{ g H}_2\text{O} \times \frac{2.016 \text{ g H}}{18.02 \text{ g H}_2\text{O}} = 0.03010 \text{ g H}$$

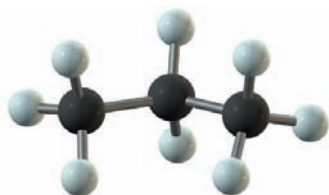
$$\text{Step 3: } \% \text{ C} = \frac{0.1346 \text{ g C}}{0.1647 \text{ g sample}} \times 100\% = 81.72\% \text{ C}$$

$$\% \text{ H} = \frac{0.03010 \text{ g H}}{0.1647 \text{ g sample}} \times 100\% = 18.28\% \text{ H}$$

$$\text{Total} = 100.00\%$$

You should now work Exercise 66.

► We could calculate the mass of H by subtracting the mass of C from the mass of the sample. It is good experimental practice, however, when possible, to base both on experimental measurements, as we have done here. This helps to check for errors in the analysis or calculation.



Can you show that the hydrocarbon in Example 2-15 is propane, C_3H_8 ?



Glucose, a simple sugar, is the main component of intravenous feeding liquids. Its common name is dextrose. It is also one of the products of carbohydrate metabolism.

When the compound to be analyzed contains oxygen, the calculation of the amount or percentage of oxygen in the sample is somewhat different. Part of the oxygen that goes to form CO_2 and H_2O comes from the sample, and part comes from the oxygen stream supplied. For that reason, we cannot directly determine the amount of oxygen already in the sample. The approach is to analyze as we did in Example 2-15 for all elements *except* oxygen. Then we subtract the sum of their masses from the mass of the original sample to obtain the mass of oxygen. The next example illustrates such a calculation.

EXAMPLE 2-16 Percent Composition

A 0.1014-g sample of purified glucose was burned in a C-H combustion train to produce 0.1486 g of CO_2 and 0.0609 g of H_2O . An elemental analysis showed that glucose contains only carbon, hydrogen, and oxygen. Determine the masses of C, H, and O in the sample and the percentages of these elements in glucose.

Plan

Steps 1 and 2: We first calculate the masses of carbon and hydrogen as we did in Example 2-15.

Step 3: The rest of the sample must be oxygen because glucose has been shown to contain only C, H, and O. So we subtract the masses of C and H from the total mass of sample.

Step 4: Then we calculate the percentage by mass for each element.

Solution

$$\text{Step 1: } \underline{\quad} \text{ g C} = 0.1486 \text{ g CO}_2 \times \frac{12.01 \text{ g C}}{44.01 \text{ g CO}_2} = 0.04055 \text{ g C}$$

$$\text{Step 2: } \underline{\quad} \text{ g H} = 0.0609 \text{ g H}_2\text{O} \times \frac{2.016 \text{ g H}}{18.02 \text{ g H}_2\text{O}} = 0.00681 \text{ g H}$$

$$\text{Step 3: } \underline{\quad} \text{ g O} = 0.1014 \text{ g sample} - [0.04055 \text{ g C} + 0.00681 \text{ g H}] = 0.0540 \text{ g O}$$

Step 4: Now we can calculate the percentages by mass for each element:

$$\% \text{ C} = \frac{0.04055 \text{ g C}}{0.1014 \text{ g}} \times 100\% = 39.99\% \text{ C}$$

$$\% \text{ H} = \frac{0.00681 \text{ g H}}{0.1014 \text{ g}} \times 100\% = 6.72\% \text{ H}$$

$$\% \text{ O} = \frac{0.0540 \text{ g O}}{0.1014 \text{ g}} \times 100\% = 53.2\% \text{ O}$$

$$\text{Total} = 99.9\%$$

You should now work Exercise 68.

► We say that the mass of O in the sample is calculated by *difference*.

2-9 Determination of Molecular Formulas

Percent composition data yield only simplest formulas. To determine the molecular formula for a molecular compound, *both* its *empirical* formula and its molecular weight must be known. Some methods for experimental determination of molecular weights are introduced in Chapters 12 and 14.

For many compounds the molecular formula is a multiple of the simplest formula. Consider butane, C_4H_{10} . The *empirical* formula for butane is C_2H_5 , but the molecular formula contains twice as many atoms; that is, $2 \times (\text{C}_2\text{H}_5) = \text{C}_4\text{H}_{10}$. Benzene, C_6H_6 , is another example. The simplest formula for benzene is CH , but the molecular formula contains six times as many atoms; that is, $6 \times (\text{CH}) = \text{C}_6\text{H}_6$.

The molecular formula for a compound is either the same as, or an *integer* multiple of, the (*empirical*) formula.

$$\text{molecular formula} = n \times \text{simplest formula}$$

So we can write

$$\text{molecular weight} = n \times \text{simplest formula weight}$$

$$n = \frac{\text{molecular weight}}{\text{simplest formula weight}}$$

The molecular formula is then obtained by multiplying the *empirical* formula by the integer, n .

EXAMPLE 2-17 Molecular Formula

In Example 2-16, we found the elemental composition of glucose. Other experiments show that its molecular weight is approximately 180 amu. Determine the simplest formula and the molecular formula of glucose.

Plan

Step 1: We first use the masses of C, H, and O found in Example 2-16 to determine the simplest formula.

► As an alternative, we could have used the percentages by mass from Example 2-16. Using the earliest available numbers helps to minimize the effects of rounding errors.

Unless otherwise noted, all content on this page is © Cengage Learning.

Step 2: We can use the simplest formula to calculate the simplest formula weight. Because the molecular weight of glucose is known (approximately 180 amu), we can determine the molecular formula by dividing the molecular weight by the simplest formula weight.

$$n = \frac{\text{molecular weight}}{\text{simplest formula weight}}$$

The molecular weight is n times the *empirical* formula weight, so the molecular *formula* of glucose is n times the *empirical formula*.

Solution

Step 1:

Element	Relative Mass of Element	Relative Number of Atoms (divide mass by AW)	Divide by Smallest	Smallest Whole-Number Ratio of Atoms
C	0.04055	$\frac{0.04055}{12.01} = 0.003376$	$\frac{0.003376}{0.003376} = 1.00$ C	CH ₂ O
H	0.00681	$\frac{0.00681}{1.008} = 0.00676$	$\frac{0.00676}{0.003376} = 2.00$ H	
O	0.0540	$\frac{0.0540}{16.00} = 0.00338$	$\frac{0.00338}{0.003376} = 1.00$ O	

STOP & THINK

The molecular formula is always the simplest formula multiplied by some positive integer; this integer can be 1.

Step 2: The simplest formula is CH₂O, which has a formula weight of 30.03 amu. Because the molecular weight of glucose is approximately 180 amu, we can determine the molecular formula by dividing the molecular weight by the *empirical* formula weight.

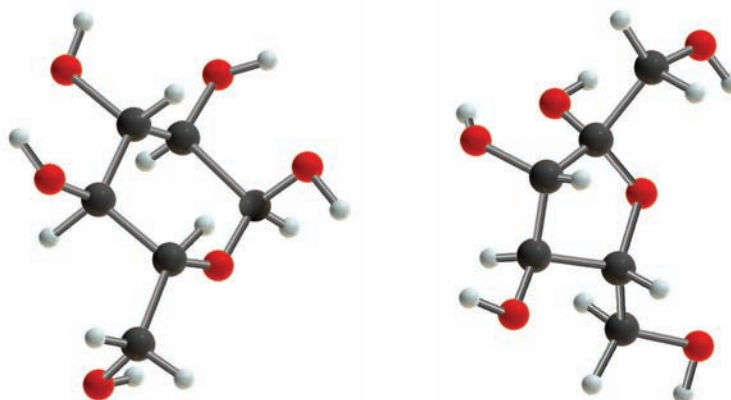
$$n = \frac{180 \text{ amu}}{30.03 \text{ amu}} = 6.00$$

The molecular weight is six times the simplest formula weight, so the molecular formula of glucose must be six times the empirical formula.

$$\text{molecular formula} = 6 \times (\text{CH}_2\text{O}) = \text{C}_6\text{H}_{12}\text{O}_6$$

You should now work Exercises 49 and 50.

► Many sugars are rich sources in our diet. The most familiar is ordinary table sugar, which is sucrose, C₁₂H₂₂O₁₁. An enzyme in our saliva readily splits sucrose into two simple sugars, glucose and fructose.



Ball-and-stick models of glucose (*left*) and fructose (*right*). Both have the formula C₆H₁₂O₆, but they have different structures and properties, so they are different compounds. Black atoms = carbon, white atoms = hydrogen, and red atoms = oxygen.

As we shall see when we discuss the composition of compounds in some detail, two (and sometimes more) elements may form more than one compound. The **Law of Multiple Proportions** summarizes many experiments on such compounds. It is usually stated:

When two elements, A and B, form more than one compound, the ratio of the masses of element B that combine with a given mass of element A in each of the compounds can be expressed by small whole numbers.

Water, H_2O , and hydrogen peroxide, H_2O_2 , provide an example. The ratio of masses of oxygen that combine with a given mass of hydrogen in H_2O and H_2O_2 is 1:2. In H_2O , one mole of oxygen combines with two moles of hydrogen atoms, while in hydrogen peroxide, H_2O_2 , two moles of oxygen combine with two moles of hydrogen atoms. Thus the ratio of oxygen atoms in the two compounds compared to a given number of hydrogen atoms is 1:2. Many similar examples, such as CO and CO_2 (1:2 oxygen ratio) and SO_2 and SO_3 (2:3 oxygen ratio), are known. The Law of Multiple Proportions had been recognized from studies of elemental composition before the time of Dalton. It provided additional support for his atomic theory.

EXAMPLE 2-18 Law of Multiple Proportions

What is the ratio of the numbers of oxygen atoms that are combined with a given number of nitrogen atoms in the compounds N_2O_3 and NO ?

Plan

To compare the number of oxygen atoms, we need to have *equal numbers of nitrogen atoms*.

Solution

Because NO has half as many nitrogen atoms in its formula relative to N_2O_3 , we must multiply it by a factor of 2 to compare the two elements on the basis of an equal number of nitrogen atoms. Once we show the number of atoms of each element present, we can cancel out the equal amounts of nitrogen atoms, leaving the ratio of oxygen atoms.

$$\text{oxygen ratio} = \frac{\text{N}_2\text{O}_3}{2(\text{NO})} = \frac{3\text{O}/\cancel{2\text{N}}}{2\text{O}/\cancel{2\text{N}}} = \frac{3\text{O}}{2\text{O}} = \frac{3}{2}$$

You should now work Exercises 71 and 72.

► In Example 2-18, we could equalize the number of N atoms by dividing N_2O_3 by a factor of two, to produce fractional subscripts, which most chemists prefer to avoid. That approach would, however, give us the same answer.

2-10 Some Other Interpretations of Chemical Formulas

Once we master the mole concept and the meaning of chemical formulas, we can use them in many ways. The examples in this section illustrate some of the other kinds of information we can get from a chemical formula and the mole concept.

EXAMPLE 2-19 Composition of Compounds

What mass of chromium is contained in 35.8 g of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$?

Plan

Let us first solve the problem in several steps.

Step 1: The formula tells us that each mole of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ contains two moles of Cr atoms, so we first find the number of moles of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, using the unit factor

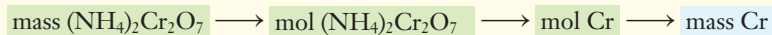
$$\frac{1 \text{ mol } (\text{NH}_4)_2\text{Cr}_2\text{O}_7}{252.0 \text{ g } (\text{NH}_4)_2\text{Cr}_2\text{O}_7}$$

► Chemists often use the term “equivalents” instead of moles when talking about the relative amounts or ratios of atoms or molecules. So Step 1 could also be written as “each equivalent of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ contains two equivalents of Cr atoms”.

Step 2: Then we convert the number of moles of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ into the number of moles of Cr atoms it contains, using the unit factor

$$\frac{2 \text{ mol Cr atoms}}{1 \text{ mol } (\text{NH}_4)_2\text{Cr}_2\text{O}_7}$$

Step 3: We then use the atomic weight of Cr to convert the number of moles of chromium atoms to the mass of chromium.



Solution

$$\begin{aligned} \text{Step 1: } \underline{} \text{ mol } (\text{NH}_4)_2\text{Cr}_2\text{O}_7 &= 35.8 \text{ g } (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \times \frac{1 \text{ mol } (\text{NH}_4)_2\text{Cr}_2\text{O}_7}{252.0 \text{ g } (\text{NH}_4)_2\text{Cr}_2\text{O}_7} \\ &= 0.142 \text{ mol } (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \end{aligned}$$

$$\begin{aligned} \text{Step 2: } \underline{} \text{ mol Cr atoms} &= 0.142 \text{ mol } (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \times \frac{2 \text{ mol Cr atoms}}{1 \text{ mol } (\text{NH}_4)_2\text{Cr}_2\text{O}_7} \\ &= 0.284 \text{ mol Cr atoms} \end{aligned}$$

$$\text{Step 3: } \underline{} \text{ g Cr} = 0.284 \text{ mol Cr atoms} \times \frac{52.0 \text{ g Cr}}{1 \text{ mol Cr atoms}} = 14.8 \text{ g Cr}$$

If you understand the reasoning in these conversions, you should be able to solve this problem in a single setup:

$$\underline{} \text{ g Cr} = 35.8 \text{ g } (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \times \frac{1 \text{ mol } (\text{NH}_4)_2\text{Cr}_2\text{O}_7}{252.0 \text{ g } (\text{NH}_4)_2\text{Cr}_2\text{O}_7} \times \frac{2 \text{ mol Cr atoms}}{1 \text{ mol } (\text{NH}_4)_2\text{Cr}_2\text{O}_7} \times \frac{52.0 \text{ g Cr}}{1 \text{ mol Cr}} = 14.8 \text{ g Cr}$$

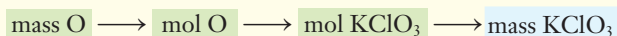
You should now work Exercise 76.

EXAMPLE 2-20 Composition of Compounds

What mass of potassium chlorate, KClO_3 , would contain 40.0 g of oxygen?

Plan

The formula KClO_3 tells us that each mole of KClO_3 contains three moles of oxygen atoms. Each mole of oxygen atoms weighs 16.0 g. So we can set up the solution to convert:



Solution

$$\begin{aligned} \underline{} \text{ g KClO}_3 &= 40.0 \text{ g O} \times \frac{1 \text{ mol O atoms}}{16.0 \text{ g O atoms}} \times \frac{1 \text{ mol KClO}_3}{3 \text{ mol O atoms}} \times \frac{122.6 \text{ g KClO}_3}{1 \text{ mol KClO}_3} \\ &= 102 \text{ g KClO}_3 \end{aligned}$$

You should now work Exercise 78.

STOP & THINK

The mass of a compound must always be greater than the mass of any element contained in the compound.

Problem-Solving Tip How Do We Know When...?

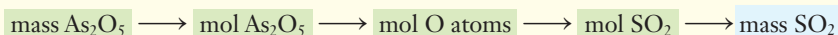
How do we know when to represent oxygen as O and when as O₂? A *compound* that contains oxygen *does not* contain O₂ molecules. So we solve problems such as Example 2-20 in terms of moles of O atoms. Thus, we must use the formula weight for O, which is 16.0 g O atoms/1 mol O atoms. Similar reasoning applies to compounds containing other elements that are polyatomic molecules in *pure elemental form*, such as H₂, Cl₂, or P₄.

EXAMPLE 2-21 Composition of Compounds

- (a) What mass of sulfur dioxide, SO₂, would contain the same mass of oxygen as is contained in 33.7 g of arsenic pentoxide, As₂O₅?
- (b) What mass of calcium chloride, CaCl₂, would contain the same number of chloride ions as are contained in 48.6 g of sodium chloride, NaCl?

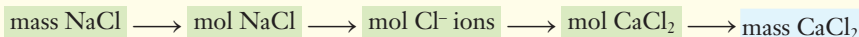
Plan

- (a) We need only convert to *moles* of O (because this is the same mass of O regardless of its environment) and then to moles of SO₂ to obtain the mass of SO₂.



Alternatively, we could find explicitly the number of grams of O in 33.7 g of As₂O₅, and then find the mass of SO₂ that contains that same number of grams of O. But this alternate method includes some unnecessary calculation.

- (b) Because one mole always consists of the same number (Avogadro's number) of items, we can reason in terms of *moles* of Cl⁻ ions and solve as in part (a).

**Solution**

$$\begin{aligned} \text{(a)} \quad \underline{} \text{ g SO}_2 &= 33.7 \text{ g As}_2\text{O}_5 \times \frac{1 \text{ mol As}_2\text{O}_5}{229.8 \text{ g As}_2\text{O}_5} \times \frac{5 \text{ mol O atoms}}{1 \text{ mol As}_2\text{O}_5} \\ &\quad \times \frac{1 \text{ mol SO}_2}{2 \text{ mol O atoms}} \times \frac{64.1 \text{ g SO}_2}{1 \text{ mol SO}_2} = \underline{23.5 \text{ g SO}_2} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \underline{} \text{ g CaCl}_2 &= 48.6 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.4 \text{ g NaCl}} \times \frac{1 \text{ mol Cl}^-}{1 \text{ mol NaCl}} \\ &\quad \times \frac{1 \text{ mol CaCl}_2}{2 \text{ mol Cl}^-} \times \frac{111.0 \text{ g CaCl}_2}{1 \text{ mol CaCl}_2} = \underline{46.2 \text{ g CaCl}_2} \end{aligned}$$

STOP & THINK

In problems such as those in Example 2-21, it is very important to use complete units. Keep track of g of *what*, mol of *what*, etc. by including them in the units.

You should now work Exercise 80.

The physical appearance of one mole of each of some compounds is illustrated in Figure 2-6. Two different forms of oxalic acid are shown. The formula unit (molecule) of oxalic acid is (COOH)₂ (FW = 90.0 amu; molar mass = 90.0 g/mol). When oxalic acid is obtained by crystallization from a water solution, however, the resulting crystals contain two molecules of water for each molecule of oxalic acid (even though it appears “dry”). The formula of this **hydrate** is (COOH)₂ · 2H₂O (FW = 126.1 amu; molar mass = 126.1 g/mol). The dot shows that the crystals contain two H₂O molecules per (COOH)₂ molecule. The water can be driven out of the crystals by heating to leave **anhydrous** oxalic acid, (COOH)₂. “Anhydrous” means “without water.” Copper(II) sulfate, an *ionic* compound,

Unless otherwise noted, all content on this page is © Cengage Learning.

shows similar behavior. Anhydrous copper(II) sulfate (CuSO_4 ; FW = 159.6 amu; molar mass = 159.6 g/mol) is almost white. Hydrated copper(II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; FW = 249.7 amu; molar mass = 249.7 g/mol) is deep blue. Example 2-22 illustrates how we might find and use the formula of a hydrate.

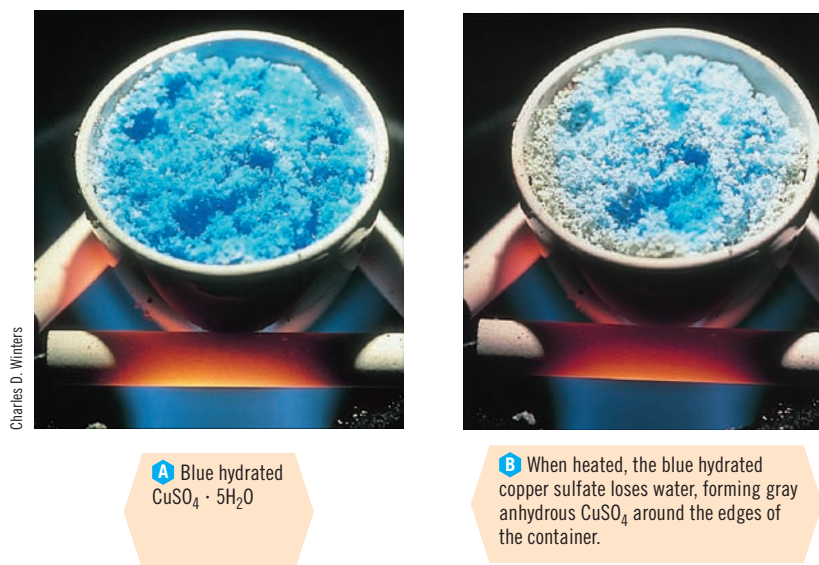


Figure 2-6 One mole of some compounds. The colorless liquid is water, H_2O (1 mol = 18.0 g). The solids are *anhydrous* oxalic acid, $(\text{COOH})_2$; *hydrated oxalic acid*, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$; hydrated copper(II) sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; and mercury(II) oxide.



EXAMPLE 2-22 Composition of Compounds

A reaction requires pure anhydrous calcium sulfate, CaSO_4 . Only an unidentified hydrate of calcium sulfate, $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$, is available.

- We heat 67.5 g of unknown hydrate until all the water has been driven off. The resulting mass of pure CaSO_4 is 53.4 g. What is the formula of the hydrate, and what is its formula weight?
- Suppose we wish to obtain enough of this hydrate to supply 95.5 g of CaSO_4 after heating. How many grams should we weigh out?

Plan

- To determine the formula of the hydrate, we must find the value of x in the formula $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$. The mass of water removed from the sample is equal to the difference in the two masses given. The value of x is the number of moles of H_2O per mole of CaSO_4 in the hydrate.
- The formula weights of CaSO_4 , 136.2 g/mol, and of $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$, $(136.2 + x18.0)$ g/mol, allow us to write the conversion factor required for the calculation.

Solution

$$(a) \quad \underline{x} \text{ g water driven off} = 67.5 \text{ g CaSO}_4 \cdot x\text{H}_2\text{O} - 53.4 \text{ g CaSO}_4 = 14.1 \text{ g H}_2\text{O}$$

$$x = \frac{\underline{x} \text{ mol H}_2\text{O}}{\text{mol CaSO}_4} = \frac{14.1 \text{ g H}_2\text{O}}{53.4 \text{ g CaSO}_4} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \times \frac{136.2 \text{ g CaSO}_4}{1 \text{ mol CaSO}_4} = \frac{2.00 \text{ mol H}_2\text{O}}{\text{mol CaSO}_4}$$

Thus, the formula of the hydrate is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Its formula weight is

$$\begin{aligned} \text{FW} &= 1 \times (\text{formula weight CaSO}_4) + 2 \times (\text{formula weight H}_2\text{O}) \\ &= 136.2 \text{ g/mol} + 2(18.0 \text{ g/mol}) = 172.2 \text{ g/mol} \end{aligned}$$

(b) The formula weights of CaSO_4 (136.2 g/mol) and of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (172.2 g/mol) allow us to write the unit factor

$$\frac{172.2 \text{ g CaSO}_4 \cdot 2\text{H}_2\text{O}}{136.2 \text{ g CaSO}_4}$$

We use this factor to perform the required conversion:

$$\begin{aligned} \underline{x} \text{ g CaSO}_4 \times 2\text{H}_2\text{O} &= 95.5 \text{ g CaSO}_4 \text{ desired} \times \frac{172.2 \text{ g CaSO}_4 \cdot 2\text{H}_2\text{O}}{136.2 \text{ g CaSO}_4} \\ &= 121 \text{ g CaSO}_4 \cdot 2\text{H}_2\text{O} \end{aligned}$$

You should now work Exercise 82.

STOP & THINK

A hydrate consists of water *plus* another substance, so the total mass of the hydrate present must always be *greater than* the mass of the other substance present.

2-11 Purity of Samples

The **percent purity** is the mass percentage of a specified substance in an impure sample. Most substances obtained from laboratory reagent shelves are not 100% pure. When impure samples are used for precise work, account must be taken of impurities. The photo in the margin shows the label from reagent-grade sodium hydroxide, NaOH, which is 98.2% pure by mass. From this information we know that total impurities represent 1.8% of the mass of this material. We can write several unit factors:

$$\frac{98.2 \text{ g NaOH}}{100 \text{ g sample}}, \quad \frac{1.8 \text{ g impurities}}{100 \text{ g sample}}, \quad \text{and} \quad \frac{1.8 \text{ g impurities}}{98.2 \text{ g NaOH}}$$

The inverse of each of these gives us a total of six unit factors.

EXAMPLE 2-23 Percent Purity

Calculate the masses of NaOH and impurities in 45.2 g of 98.2% pure NaOH.

Plan

The percentage of NaOH in the sample gives the unit factor $\frac{98.2 \text{ g NaOH}}{100 \text{ g sample}}$. The remainder of the sample is $100\% - 98.2\% = 1.8\%$ impurities; this gives the unit factor $\frac{1.8 \text{ g impurities}}{100 \text{ g sample}}$.

Solution

$$\underline{x} \text{ g NaOH} = 45.2 \text{ g sample} \times \frac{98.2 \text{ g NaOH}}{100 \text{ g sample}} = 44.4 \text{ g NaOH}$$

$$\underline{x} \text{ g impurities} = 45.2 \text{ g sample} \times \frac{1.8 \text{ g impurities}}{100 \text{ g sample}} = 0.81 \text{ g impurities}$$

You should now work Exercises 86 and 87.

ACTUAL ANALYSIS, LOT G22931		
Meets A.C.S. Specifications	98.2	%
Assay (NaOH) (by acidimetry)	0.2	%
Sodium Carbonate (Na_2CO_3)	< 0.0005	%
Chloride (Cl)	< 0.01	%
Ammonium Hydroxide Precipitate	< 0.0005	%
Heavy Metals (as Ag)	0.0003	%
Copper (Cu)	0.002	%
Potassium (K) (by FES)	< 2	
Trace Impurities (in ppm):		
Nitrogen Compounds (as N)	< 1	
Phosphate (PO_4)	< 5	
Sulfate (SO_4)	< 2	
Iron (Fe)	< 0.003	
Mercury (Hg) (by AAS)	< 2	
Nickel (Ni)	< 2	

A label from a bottle of sodium hydroxide, NaOH

► Impurities are not necessarily bad. For example, inclusion of 0.02% KI, potassium iodide, in ordinary table salt has nearly eliminated goiter in the United States. Goiter is a disorder of the thyroid gland caused by a deficiency of iodine. Mineral water tastes better than purer, distilled water.

Unless otherwise noted, all content on this page is © Cengage Learning.

Problem-Solving Tip Utility of the Unit Factor Method

Observe the beauty of the unit factor approach to problem solving! Such questions as “do we multiply by 0.982 or divide by 0.982?” never arise. The units always point toward the correct answer because we use unit factors constructed so that units *always* cancel out and we arrive at the desired unit.

Many important relationships have been introduced in this chapter. Some of the most important transformations you have seen in Chapters 1 and 2 are summarized in Figure 2-7.

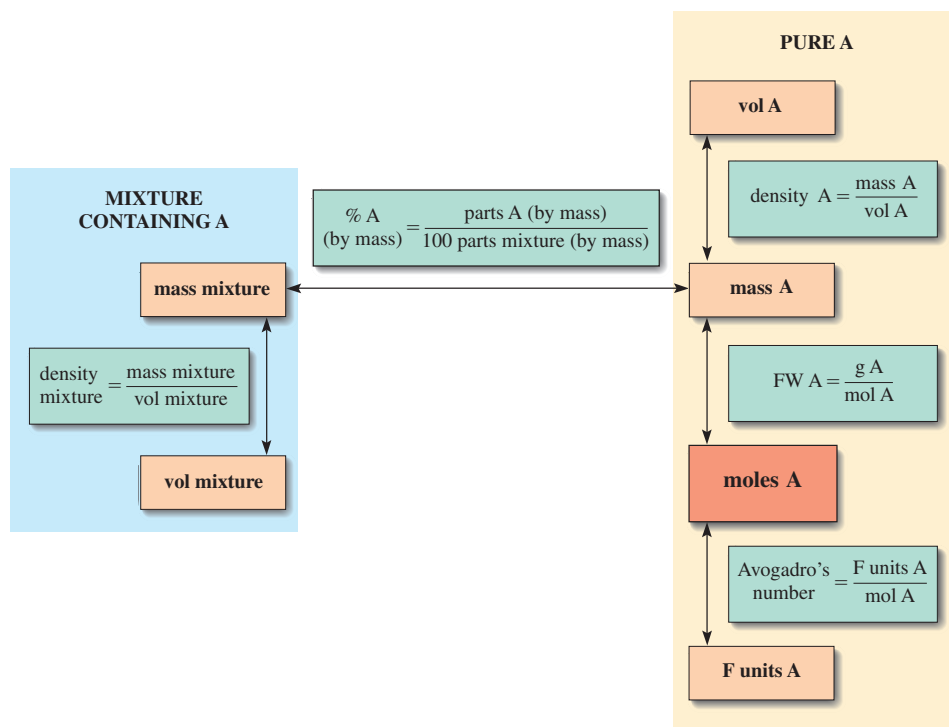


Figure 2-7 Some important relationships from Chapters 1 and 2. The relationships that provide unit factors are enclosed in green boxes. F units = formula units (molecules for molecular systems).

KEY TERMS

Allotropic modifications (allotropes) Different structural forms of the same element.

Anhydrous Without water.

Anion An ion with a negative charge.

Atomic mass unit (amu) One-twelfth of the mass of an atom of the carbon-12 isotope; a unit used for stating atomic and formula weights.

Atomic weight Weighted average of the masses of the constituent isotopes of an element; the relative mass of atoms of different elements.

Avogadro's number 6.022×10^{23} units of a specified item. See *Mole*.

Cation An ion with a positive charge.

Chemical formula Combination of element symbols that indicates the chemical composition of a substance.

Composition stoichiometry Describes the quantitative (mass) relationships among elements in compounds.

Empirical formula See *Simplest formula*.

Formula Combination of element symbols that indicates the chemical composition of a substance.

Formula unit The smallest repeating unit of a substance—for non-ionic substances, the molecule.

Formula weight The mass, in atomic mass units, of one formula unit of a substance. Numerically equal to the mass, in grams, of one mole of the substance (see *Molar mass*). This number is obtained by adding the atomic weights of the atoms specified in the formula.

Hydrate A crystalline sample that contains water, H_2O , and another compound in a fixed mole ratio. Examples include $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$.

Ion An atom or group of atoms that carries an electric charge.

A positive ion is a *cation*; a negative ion is an *anion*.

Ionic compound A compound that is composed of cations and anions. An example is sodium chloride, NaCl.

Law of Constant Composition See *Law of Definite Proportions*.

Law of Definite Proportions Different samples of a pure compound always contain the same elements in the same proportions by mass; this corresponds to atoms of these elements in fixed numerical ratios. Also known as the Law of Constant Composition.

Law of Multiple Proportions When two elements, A and B, form more than one compound, the ratio of the masses of element B that combine with a given mass of element A in each of the compounds can be expressed by small whole numbers.

Molar mass The mass, in grams, of one mole of a substance; numerically equal to the formula weight of the substance. See *Formula weight*; see *Molecular weight*.

Mole 6.022×10^{23} (Avogadro's number of) formula units (or molecules, for a molecular substance) of a substance. The mass, in grams, of one mole is numerically equal to the formula (molecular) weight of the substance.

Molecular formula A formula that indicates the actual number of atoms present in a molecule of a molecular substance. Compare with *Simplest (empirical) formula*.

Molecular weight The mass, in atomic mass units, of one molecule of a non-ionic (molecular) substance. Numerically equal to the mass, in grams, of one mole of such a substance. This number is obtained by adding the atomic weights of the atoms specified in the formula.

Percent composition The mass percentage of each element in a compound.

Percent purity The mass percentage of a specified compound or element in an impure sample.

Polyatomic Consisting of more than one atom. Elements such as Cl₂, P₄, and S₈ exist as polyatomic molecules. Examples of polyatomic ions are the ammonium ion, NH₄⁺, and the sulfate ion, SO₄²⁻.

Simplest formula The smallest whole-number ratio of atoms present in a compound; also called *empirical formula*. Compare with *Molecular formula*.

Stoichiometry Description of the quantitative relationships among elements in compounds (composition stoichiometry) and among substances as they undergo chemical changes (reaction stoichiometry).

Structural formula A representation that shows how atoms are connected in a compound.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Basic Ideas

- (a) Define "stoichiometry." (b) Distinguish between composition stoichiometry and reaction stoichiometry.
- Give two examples of molecules that represent allotropes. Which of the compounds you selected are diatomic?
- List the common ions present in each of the formula units: (a) MgCl₂; (b) (NH₄)₂CO₃; (c) Zn(NO₃)₂.
- Draw the structural formulas and the ball-and-stick models of water and ethanol (CH₃CH₂OH). What arrangement of atoms is alike in these two compounds?
- Draw the space-filling and ball-and-stick models of ethanol (CH₃CH₂OH) and methanol (CH₃OH). What structural features do they have in common?
- What structural feature distinguishes organic compounds from inorganic compounds? Draw a molecular model of an organic compound and an inorganic compound.
- Give the names and formulas of the compounds in Table 2-1 that are organic compounds.
- Select a compound from Table 2-1 that contains only carbon and hydrogen and is not one of the compounds in Figure 1-5. Draw a ball-and-stick model of the selected compound.

- Select a compound from Table 2-1 that contains carbon, hydrogen and oxygen and is not one of the compounds in Figure 1-5. Draw a ball-and-stick model of the selected compound.
- Give examples of molecules that contain (a) three atoms of oxygen; (b) only two atoms of hydrogen; (c) four atoms total; (d) eight atoms total; (e) eight atoms of hydrogen.
- Define the following terms: (a) formula weight (or formula mass); (b) molecular weight (or molecular mass); (c) structural formula; (d) ion.

Names and Formulas

- Name the following compounds: (a) HNO₃; (b) C₅H₁₂; (c) NH₃; (d) CH₃OH.
- Write formulas for the following compounds: (a) butane; (b) ethyl alcohol; (c) sulfur trioxide; (d) acetone; (e) carbon tetrachloride.
- Write the chemical symbol for each of the following ions. Classify each as a monatomic or polyatomic ion. Classify each as a cation or an anion. (a) magnesium ion; (b) sulfite ion; (c) copper(I) ion; (d) ammonium ion; (e) oxide ion.

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

15. Name each of the following compounds: (a) MgCl_2 ; (b) $\text{Fe}(\text{NO}_3)_2$; (c) Na_2SO_4 ; (d) $\text{Ca}(\text{OH})_2$; (e) FeSO_4 .
16. Determine the chemical formulas for barium sulfate, magnesium nitrate, and sodium acetate. Each compound contains a monatomic cation and a polyatomic anion. What are the names and electrical charges of these ions?
17. Write the chemical formula for the ionic compound formed between each of the following pairs of ions. Name each compound. (a) Na^+ and OH^- ; (b) Al^{3+} and CO_3^{2-} ; (c) Na^+ and PO_4^{3-} ; (d) Ca^{2+} and NO_3^- ; (e) Fe^{2+} and CO_3^{2-} .
18. Write the chemical formula for the ionic compound formed between each of the following pairs of ions. Name each compound. (a) Cu^{2+} and CO_3^{2-} ; (b) Sr^{2+} and Br^- ; (c) NH_4^+ and CO_3^{2-} ; (d) Zn^{2+} and O^{2-} ; (e) Fe^{3+} and SO_4^{2-} .
19. A student was asked to write the chemical formulas for the following compounds. If the formulas are correct, say so. Explain why any that are incorrect are in error, and correct them. (a) potassium iodide, PI ; (b) copper(I) nitrate, CuNO_3 ; (c) silver carbonate, AgCO_4 .
20. Convert each of the following into a correct formula represented with correct notation: (a) NaCO_3 ; (b) Mg_2Cl ; (c) $\text{Zn}(\text{OH})_3$; (d) $(\text{NH}_4)_3\text{S}$; (e) $\text{Na}_2(\text{I})_2$.
21. Convert each of the following into a correct formula represented with correct notation: (a) AlO_3H_3 ; (b) Mg_3CO_3 ; (c) $\text{Zn}(\text{CO}_3)_2$; (d) $(\text{NH}_4)_3\text{SO}_4$; (e) $\text{Zn}_2(\text{SO}_4)_2$.
22. Write the formula of the compound produced by the combination of each of the following pairs of elements. Name each compound. (a) sodium and bromine; (b) magnesium and bromine; (c) sulfur and oxygen; (d) calcium and oxygen; (e) potassium and sulfur; (f) aluminum and bromine.



Aluminum reacting with bromine

23. Write the chemical formula of each of the following: (a) calcium carbonate—major component of coral, seashells, and limestone—found in antacid preparations; (b) magnesium hydroxide—found in milk of magnesia; (c) acetic acid—the acid in vinegar; (d) sodium hydroxide—common name is lye; (e) zinc oxide—used

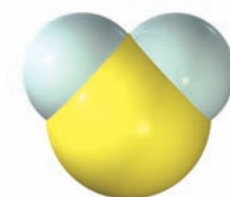
to protect from sunlight's UV rays when blended in an ointment.



Zinc oxide used as a sunscreen

Atomic and Formula Weights

24. What is the mass ratio (four significant figures) of one atom of Rb to one atom of Br?
25. An atom of an element has a mass ever so slightly greater than twice the mass of an Ni atom. Identify the element.
26. (a) What is the atomic weight of an element? (b) Why can atomic weights be referred to as relative numbers?
27. (a) What is the atomic mass unit (amu)? (b) The atomic weight of aluminum is 26.98 amu, and the atomic weight of cobalt is 58.93 amu. What can we say about the relative masses of Al and Co atoms?
28. Determine the formula weight (molecular mass) of each of the following substances: (a) bromine, Br_2 ; (b) hydrogen peroxide, H_2O_2 ; (c) saccharin, $\text{C}_7\text{H}_5\text{NSO}_3$; (d) potassium chromate, K_2CrO_4 .
29. Determine the formula weight (molecular mass) of each of the following substances: (a) calcium sulfate, CaSO_4 ; (b) propane, C_3H_8 ; (c) the sulfa drug sulfanilamide, $\text{C}_6\text{H}_4\text{SO}_2(\text{NH}_2)_2$; (d) uranyl phosphate, $(\text{UO}_2)_3(\text{PO}_4)_2$.
30. Determine the formula weight (molecular mass) of each of the following common acids:



A hydrogen sulfide



B phosphorus trichloride



C hypochlorous acid

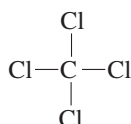


D hydrogen iodide

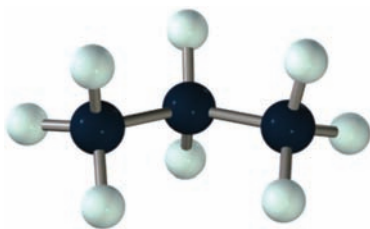
31. A sample of 1.76 g of barium combines exactly with 0.487 g of fluorine, forming barium fluoride, BaF_2 . Find the relative masses of the atoms of barium and fluorine. Check your answer using a table of atomic weights. If the formula were not known, could you still do this calculation?

The Mole Concept

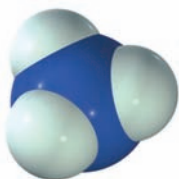
32. Calculate the mass in grams and kilograms of 2.371 moles of



33. What mass, in grams, should be weighed for an experiment that requires 1.24 mol of $\text{H}-\text{O}-\text{O}-\text{H}$?
 34. How many hydrogen atoms are contained in 167 grams of propane?



35. (a) How many formula units are contained in 154.3 g of K_2CrO_4 ? (b) How many potassium ions? (c) How many CrO_4^{2-} ions? (d) How many atoms of all kinds?
 36. How many moles of NH_3 are in a 12.50-gram sample?



37. A large neon sign is to be filled with a mixture of gases, including 6.438 g neon. What number of moles is this?



Charles D. Winters

Neon discharge tube

38. How many molecules are in 31.6 g of each of the following substances? (a) CO_2 ; (b) N_2 ; (c) P_4 ; (d) P_2 . (e) Do parts (c) and (d) contain the same number of atoms of phosphorus?
 39. Sulfur molecules exist under various conditions as S_8 , S_6 , S_4 , S_2 , and S . (a) Is the mass of one mole of each of these molecules the same? (b) Is the number of molecules in one mole of each of these molecules the same? (c) Is the mass of sulfur in one mole of each of these molecules the same? (d) Is the number of atoms of sulfur in one mole of each of these molecules the same?
 40. Complete the following table. Refer to a table of atomic weights.

Element	Atomic Weight	Mass of One Mole of Atoms
(a) Sn		
(b)	79.904	
(c) Mg		
(d)		51.9961 g

41. Complete the following table. Refer to a table of atomic weights.

Element	Formula	Mass of One Mole of Molecules
(a) Br	Br_2	
(b)	O_2	
(c)	P_4	
(d)		20.1797 g
(e) S		256.528 g
(f) O		

42. Complete the following table.

Moles of Compound	Moles of Cations	Moles of Anions
1 mol NaClO_4		
2 mol K_2SO_4		
0.2 mol calcium sulfate		
	0.50 mol NH_4^+	0.25 mol SO_4^{2-}

43. What is the average mass of one copper atom?
 44. What is the mass of 6.00 million methane, CH_4 , molecules?
 45. A sample of propane, C_3H_8 , has the same mass as 8.00 million molecules of methane, CH_4 . How many C_3H_8 molecules does the sample contain?
 46. Referring to the compounds in Exercise 30, which will contain the largest number of moles of atoms per 100.0 grams of compound?

Composition Stoichiometry

47. What percent by mass of iron(II) phosphate is iron?
 48. Calculate the percent by mass of silver found in a particular mineral that is determined to be silver carbonate.

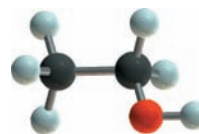
49. ● An alcohol is 60.00% C, 13.33% H, and 26.67% O by mass. Another experiment shows that its molecular weight (mass) is approximately 60 amu. What is the molecular formula of the alcohol?
50. Skatole is found in coal tar and in human feces. It contains three elements: C, H, and N. It is 82.40% C and 6.92% H by mass. Its simplest formula is its molecular formula. What are (a) the formula and (b) the molecular weight of skatole?
51. Testosterone, the male sex hormone, contains only C, H, and O. It is 79.12% C and 9.79% H by mass. Each molecule contains two O atoms. What are (a) the molecular weight and (b) the molecular formula for testosterone?
52. ▲ The beta-blocker drug, timolol, is expected to reduce the need for heart bypass surgery. Its composition by mass is 49.4% C, 7.64% H, 17.7% N, 15.2% O, and 10.1% S. The mass of 0.0100 mol of timolol is 3.16 g. (a) What is the simplest formula of timolol? (b) What is the molecular formula of timolol?
53. Determine the simplest formula for each of the following compounds: (a) copper(II) tartrate: 30.03% Cu, 22.70% C, 1.91% H, 45.37% O; (b) nitrosyl fluoroborate: 11.99% N, 13.70% O, 9.25% B, 65.06% F.
54. The hormone norepinephrine is released in the human body during stress and increases the body's metabolic rate. Like many biochemical compounds, norepinephrine is composed of carbon, hydrogen, oxygen, and nitrogen. The percent composition of this hormone is 56.8% C, 6.56% H, 28.4% O, and 8.28% N. What is the simplest formula of norepinephrine?
55. (a) A sample of a compound is found to contain 5.60 g N, 14.2 g Cl, and 0.800 g H. What is the simplest formula of this compound? (b) A sample of another compound containing the same elements is found to be 26.2% N, 66.4% Cl, and 7.5% H. What is the simplest formula of this compound?
56. A common product found in nearly every kitchen contains 27.37% sodium, 1.20% hydrogen, 14.30% carbon, and 57.14% oxygen. The simplest formula is the same as the formula of the compound. Find the formula of this compound.
57. Bupropion is present in a medication that is an antidepressant and is also used to aid in quitting smoking. The composition of bupropion is 65.13% carbon, 7.57% hydrogen, 14.79% chlorine, 5.84% nitrogen, and 6.67% oxygen. The simplest formula is the same as the molecular formula of this compound. Determine the formula.
58. Lysine is an essential amino acid. One experiment showed that each molecule of lysine contains two nitrogen atoms. Another experiment showed that lysine contains 19.2% N, 9.64% H, 49.3% C, and 21.9% O by mass. What is the molecular formula for lysine?
59. Cocaine has the following percent composition by mass: 67.30% C, 6.930% H, 21.15% O, and 4.62% N. What is the simplest formula of cocaine?
60. A compound with the molecular weight of 56.0 g was found as a component of photochemical smog. The compound is composed of carbon and oxygen, 42.9%

and 57.1%, respectively. What is the formula of this compound?

61. Calculate the percent composition of each of the following compounds: (a) aspartame, $C_{14}H_{18}N_2O_5$; (b) carborundum, SiC; (c) aspirin, $C_9H_8O_4$.
62. Calculate the percent composition of each of the following compounds: (a) L-DOPA, $C_9H_{11}NO_4$; (b) vitamin E, $C_{29}H_{50}O_2$; (c) vanillin, $C_8H_8O_3$.

Determination of Simplest and Molecular Formulas

63. ● Write the chemical formula and the simplest formula of each of the following compounds: (a) hydrogen peroxide; (b) water; (c) ethylene glycol.
64. ▲ Copper is obtained from ores containing the following minerals: azurite, $Cu_3(CO_3)_2(OH)_2$; chalcocite, Cu_2S ; chalcopyrite, $CuFeS_2$; covellite, CuS ; cuprite, Cu_2O ; and malachite, $Cu_2CO_3(OH)_2$. Which mineral has the lowest copper content as a percent by mass?
65. A 1.20-g sample of a compound gave 2.92 g of CO_2 and 1.22 g of H_2O on combustion in oxygen. The compound is known to contain only C, H, and O. What is its simplest formula?
66. A 0.1153-gram sample of a pure hydrocarbon was burned in a C—H combustion train to produce 0.3986 gram of CO_2 and 0.0578 gram of H_2O . Determine the masses of C and H in the sample and the percentages of these elements in this hydrocarbon.
67. Dimethylhydrazine, the fuel used in the Apollo lunar descent module, has a molar mass of 60.10 g/mol. It is made up of carbon, hydrogen, and nitrogen atoms. The combustion of 3.302 g of the fuel in excess oxygen yields 4.839 g of carbon dioxide and 3.959 g of water. What are the simplest and molecular formulas for dimethylhydrazine?
68. ● What is the maximum mass of carbon dioxide that can be produced by the combustion of 0.377 g of the following compound?



69. ▲ Complicated chemical reactions occur at hot springs on the ocean floor. One compound obtained from such a hot spring consists of Mg, Si, H, and O. From a 0.301-g sample, the Mg is recovered as 0.104 g of MgO ; H is recovered as 23.1 mg of H_2O ; and Si is recovered as 0.155 g of SiO_2 . What is the simplest formula of this compound?
70. A 1.000-gram sample of an alcohol was burned in oxygen to produce 1.913 g of CO_2 and 1.174 g of H_2O . The alcohol contained only C, H, and O. What is the simplest formula of the alcohol?

The Law of Multiple Proportions

71. Show that the compounds water, H_2O , and hydrogen peroxide, H_2O_2 , obey the Law of Multiple Proportions.

72. Nitric oxide, NO, is produced in internal combustion engines. When NO comes in contact with air, it is quickly converted into nitrogen dioxide, NO₂, a very poisonous, corrosive gas. What mass of O is combined with 3.00 g of N in (a) NO and (b) NO₂? Show that NO and NO₂ obey the Law of Multiple Proportions.
73. A certain metal, M, forms two oxides, M₂O and MO. If the percent by mass of M in M₂O is 73.4%, what is its percent by mass in MO?
74. What mass of oxygen is combined with 9.04 g of sulfur in (a) sulfur dioxide, SO₂, and (b) sulfur trioxide, SO₃?

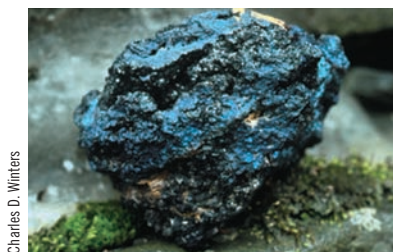
Interpretation of Chemical Formulas

75. One prominent ore of copper contains chalcopyrite, CuFeS₂. How many pounds of copper are contained in 6.63 pounds of pure CuFeS₂?
76. Mercury occurs as a sulfide ore called *cinnabar*, HgS. How many grams of mercury are contained in 578 g of pure HgS?



A sample of cinnabar

77. (a) How many grams of copper are contained in 253 g of CuSO₄? (b) How many grams of copper are contained in 573 g of CuSO₄ · 5H₂O?
78. What mass of KMnO₄ would contain 72.6 g of manganese?
79. What mass of azurite, Cu₃(CO₃)₂(OH)₂, would contain 685 g of copper?



A sample of azurite

80. Two minerals that contain copper are chalcopyrite, CuFeS₂, and chalcocite, Cu₂S. What mass of chalcocite would contain the same mass of copper as is contained in 418 pounds of chalcopyrite?
81. Tungsten is a very dense metal (19.3 g/cm³) with extremely high melting and boiling points (3370°C and 5900°C). When a small amount of it is included in steel, the resulting alloy is far harder and stronger than ordinary steel. Two important ores of tungsten are FeWO₄ and CaWO₄. How many grams of CaWO₄ would contain the same mass of tungsten that is present in 657 g of FeWO₄?

82. ▲ When a mole of CuSO₄ · 5H₂O is heated to 110°C, it loses four moles of H₂O to form CuSO₄ · H₂O. When it is heated to temperatures above 150°C, the other mole of H₂O is lost. (a) How many grams of CuSO₄ · H₂O could be obtained by heating 495 g of CuSO₄ · 5H₂O to 110°C? (b) How many grams of anhydrous CuSO₄ could be obtained by heating 463 g of CuSO₄ · 5H₂O to 180°C?

Percent Purity

83. A particular ore of lead, galena, is 10.0% lead sulfide, PbS, and 90.0% impurities by weight. What mass of lead is contained in 110.5 grams of this ore?



A sample of galena

84. What mass of chromium is present in 234 grams of an ore of chromium that is 55.0% iron(II) dichromate, FeCr₂O₇, and 45.0% impurities by mass? If 90.0% of the chromium can be recovered from 400.0 grams of the ore, what mass of pure chromium is obtained?
85. What masses of (a) Sr and (b) N are contained in 267.7 g of 88.2% pure Sr(NO₃)₂? Assume that the impurities do not contain the elements mentioned.
86. (a) What weight of magnesium carbonate is contained in 275 pounds of an ore that is 26.7% magnesium carbonate by weight? (b) What weight of impurities is contained in the sample? (c) What weight of magnesium is contained in the sample? (Assume that no magnesium is present in the impurities.)
87. Vinegar is 5.0% acetic acid, C₂H₄O₂, by mass. (a) How many grams of acetic acid are contained in 143.7 g of vinegar? (b) How many pounds of acetic acid are contained in 143.7 pounds of vinegar? (c) How many grams of sodium chloride, NaCl, are contained in 34.0 g of saline solution that is 5.0% NaCl by mass?
88. ▲ What is the percent by mass of copper sulfate, CuSO₄, in a sample of copper sulfate pentahydrate, CuSO₄ · 5H₂O? (b) What is the percent by mass of CuSO₄ in a sample that is 74.4% CuSO₄ · 5H₂O by mass?

Mixed Examples

89. Ammonium sulfate, (NH₄)₂SO₄, and urea, CH₄N₂O, are both commonly used as sources of nitrogen in commercial fertilizers. If ammonium sulfate costs \$7.00 for 20 lb and urea costs \$21.00 for 6 lb, which has the more nitrogen for the dollar?
90. (a) How many moles of ozone molecules are contained in 96.0 g of ozone, O₃? (b) How many moles of oxygen atoms



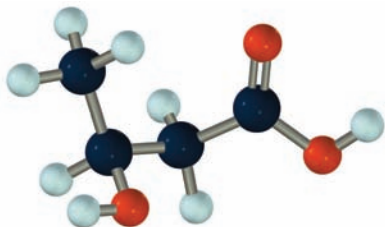
- are contained in 96.0 g of ozone? (c) What mass of O_2 would contain the same number of oxygen atoms as 96.0 g of ozone? (d) What mass of oxygen gas, O_2 , would contain the same number of molecules as 96.0 g of ozone?
91. The recommended daily dietary allowance of calcium is 1200 mg. Calcium carbonate is an inexpensive source of calcium and useful as a dietary supplement as long as it is taken along with vitamin D, which is essential to calcium absorption. How many grams of calcium carbonate must an individual take per day to provide for his/her recommended daily allowance of calcium?
 92. Vitamin E is an antioxidant that plays an especially important role protecting cellular structures in the lungs. Combustion of a 0.497-g sample of vitamin E produced 1.47 g of carbon dioxide and 0.518 g of water. Determine the empirical formula of vitamin E.
 93. A metal, M, forms an oxide having the simplest formula M_2O_3 . This oxide contains 52.9% of the metal by mass. (a) Calculate the atomic weight of the metal. (b) Identify the metal.
 94. Three samples of magnesium oxide were analyzed to determine the mass ratios O/Mg, giving the following results:

$\frac{1.60 \text{ g O}}{2.43 \text{ g Mg}}$;	$\frac{0.658 \text{ g O}}{1.00 \text{ g Mg}}$;	$\frac{2.29 \text{ g O}}{3.48 \text{ g Mg}}$
--	---	--

 Which law of chemical combination is illustrated by these data?
 95. ▲ The molecular weight of hemoglobin is about 65,000 g/mol. Hemoglobin contains 0.35% Fe by mass. How many iron atoms are in a hemoglobin molecule?
 96. ▲ More than 1 billion pounds of adipic acid (MW 146.1 g/mol) is manufactured in the United States each year. Most of it is used to make synthetic fabrics. Adipic acid contains only C, H, and O. Combustion of a 1.6380-g sample of adipic acid gives 2.960 g of CO_2 and 1.010 g of H_2O . (a) What is the simplest formula for adipic acid? (b) What is its molecular formula?
 97. Crystals of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, provide the hardness associated with bones. In hydroxyapatite crystals, what is (a) the percent calcium and (b) the percent phosphorus?

Conceptual Exercises

98. ● In 2003 researchers at Columbia University demonstrated that β -hydroxybutyric acid may be a cheap and easy way to treat Parkinson's disease. From the molecular model shown below determine the structural formula and the chemical formula of β -hydroxybutyric acid. (Color code: black = carbon, white = hydrogen, red = oxygen.)



- In a structural formula, each line connecting two chemical symbols represents a pair of electrons that is shared between the two atoms. Based upon your examination of this and other structures in this chapter, how many pairs of electrons does a carbon atom generally share with other atoms? Does an oxygen atom or a hydrogen atom share this same number of pairs of electrons with other atoms?
99. For each of the following simple ions, locate the element on the periodic table: Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and Al^{3+} . There is a pattern here. How is the charge of a cation related to the group number (the label at the top of the column)? What charge is a cation formed from a rubidium atom likely to have? Write the formula for the cation formed from a barium atom. Locate the elements that form the following anions on the periodic table: F^- , Cl^- , Br^- , I^- , O^{2-} , and S^{2-} . What is the formula for the anion formed from a nitrogen atom?
 100. Determine what is wrong with the formula for each of the following substances. Then write the correct formula.

lithium fluoride, LiF_2
 iron(III) sulfide, Fe_3S
 aluminum hydroxide, $AlOH_3$
 zinc nitrate, $Zn_3(NO)_2$
 calcium chloride, $CaCl^+$
 101. Currently, Avogadro's number is defined as the number of "atoms in exactly 0.012 kg of pure carbon-12," which has been measured to be approximately 6.0221479×10^{23} , depending upon the stability of the standard kilogram. R. F. Fox and T. P. Hill (American Scientist, March–April 2007, 104) have proposed that it be defined as an integer, namely 84,446,888³ or 602,214,141,070,409,084,099,072, exactly. How different is this number from the current value? The mass of the standard kilogram may have changed about 50 μg since it was constructed. That's roughly 150 quadrillion (1.5×10^{17}) atoms of platinum and iridium. How does this uncertainty compare with the difference between the two values for Avogadro's number?
 102. Calculate the percentage by mass of rhenium, Re, in each of the following oxides: ReO_2 , ReO_3 , Re_2O_3 , Re_2O_7 . Determine the charge that rhenium has in each of these compounds. Arrange the formulas in order of increasing charge on the rhenium ion. How does the percentage of rhenium in these oxides change as the charge of the rhenium ion changes?
 103. Some compounds with different molecular formulas have the same empirical formula. Acetic acid, CH_3COOH , is found in vinegar. Erythrose, $HOCH_2COCH(OH)CH_2OH$, is used in sunless tanning products. Embalming fluids may contain formaldehyde, H_2CO . An important component of sour milk and sore muscles is lactic acid, $CH_3CH(OH)COOH$. Ribose, $HOCH_2CH(OH)CH(OH)CH(OH)CHO$, is an important part of ribonucleic acid. Determine the molecular and empirical formulas for each of these compounds, listing the elements in this order: carbon, hydrogen, and oxygen. Calculate the molecular weight of each compound. What is the ratio of each of the molecular weights to the formula weight of the empirical formula?

104. If a 3.2-mole sample of each of the following compounds is completely burned, which one would produce the most moles of water? Which would produce the fewest? (a) $\text{CH}_3\text{CH}_2\text{OH}$; (b) CH_3OH ; (c) CH_3OCH_3 .
105. When a sample is burned in a combustion train, the percent oxygen in the sample cannot be determined directly from the mass of water and carbon dioxide formed. Why?
106. What mass of NaCl would contain the same *total* number of ions as 284 g of MgCl_2 ?
107. Two deposits of minerals containing silver are found. One of the deposits contains silver oxide, and the other contains silver sulfide. The deposits can be mined at the same price per ton of the original silver-containing compound, but only one deposit can be mined by your company. Which of the deposits would you recommend and why?
108. A decision is to be made as to the least expensive source of zinc. One source of zinc is zinc sulfate, ZnSO_4 , and another is zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. These two sources of zinc can be purchased at the same price per kilogram of compound. Which is the most economical source of zinc and by how much?
109. Assume that a penny is $1/16$ in. thick and that the moon is 222,000 mi at its closest approach to the earth (perigee). Show by calculation whether or not a picomole of pennies stacked on their faces would reach from the earth to the moon.
110. Calculate the mass in grams of 13.5 mol of (a) vinyl chloride, $\text{C}_2\text{H}_3\text{Cl}$, the starting material for a plastic; (b) capsaicin, $\text{C}_{18}\text{H}_{27}\text{NO}_3$, the substance that makes red chili peppers “hot”; (c) stearic acid, $\text{C}_{18}\text{H}_{36}\text{O}_2$, used in soaps.
- 1.114 g of CO_2 and 0.455 g of water. An independent analysis indicated that the molar mass of the compound is 74.1 g/mol. What are the empirical and molecular formulas of this compound?
113. Elemental lead is needed in the construction of storage batteries. The lead is obtained by first roasting galena (PbS) in limited air to produce sulfur dioxide and lead oxide. The lead oxide formed is 92.83% lead. The lead is then obtained from the lead oxide in a process that is nearly 100% efficient. What is the simplest formula of the lead oxide formed?
114. Near room temperature, the density of water is 1.00 g/mL, and the density of ethanol (grain alcohol) is 0.789 g/mL. What volume of ethanol contains the same number of molecules as are present in 380. mL of H_2O ?
115. A drop of water has a volume of about 0.050 mL. How many molecules of water are in a drop of water? (Assume water has a density of 1.00 g/cm³.)
116. Use the molecular volume provided with each compound to calculate its density in g/mL: (a) NaHCO_3 , sodium bicarbonate or sodium hydrogen carbonate (also called baking soda), 0.0389 L/mol; (b) I_2 , iodine, 0.05148 L/mol; (c) Hg, liquid mercury, 0.01476 L/mol; (d) NaCl , common table salt, 0.02699 L/mol.

Beyond the Textbook

NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.*

Building Your Knowledge

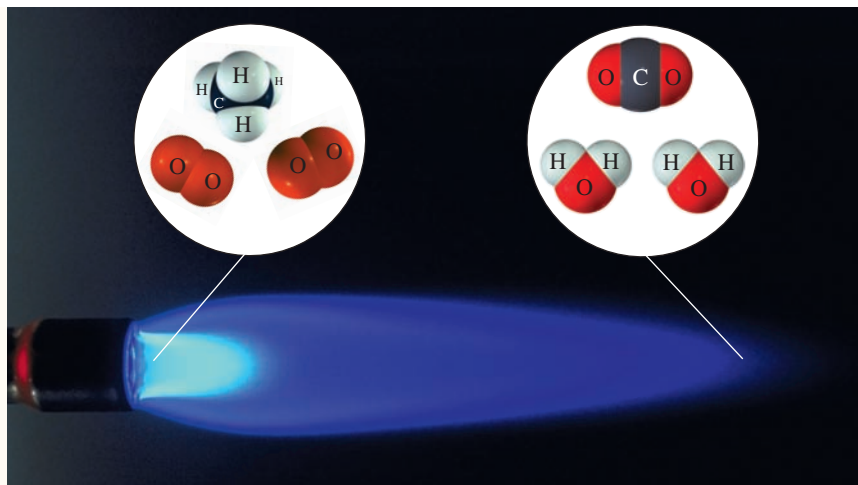
NOTE: *Beginning with this chapter, exercises under the “Building Your Knowledge” heading will often require that you use skills, concepts, or information that you should have mastered in earlier chapters. This provides you an excellent opportunity to “tie things together” as you study.*

111. Vegetarians sometimes suffer from the lack of vitamin B12. Each molecule of vitamin B12 contains a single atom of cobalt and is 4.35% cobalt by mass. What is the molecular weight of vitamin B12?
112. A student wants to determine the empirical and molecular formulas of a compound containing only carbon, hydrogen, and oxygen. To do so, he combusted a 0.625-g sample of the compound and collected
117. Use an internet search engine (such as <http://www.google.com>) to locate the history and properties of the element zinc. When was it first isolated? What are three common uses of zinc? Describe the reported effects of a zinc deficiency in one’s diet.
118. Use an internet search engine (such as <http://www.google.com>) to locate the history and properties of the element iodine. When was it first isolated? What are three common uses of iodine? Describe three health effects associated with iodine or iodine-containing compounds.
119. Use an internet search engine (such as <http://www.google.com>) to locate a source of chemistry jokes or puns. Quote a joke or pun that involves the name of an element. Quote a joke or pun that involves a low formula weight compound.
120. Use an internet search engine (such as <http://www.google.com>) to locate the history of Louis Joseph Gay-Lussac. Which element did he discover and isolate?



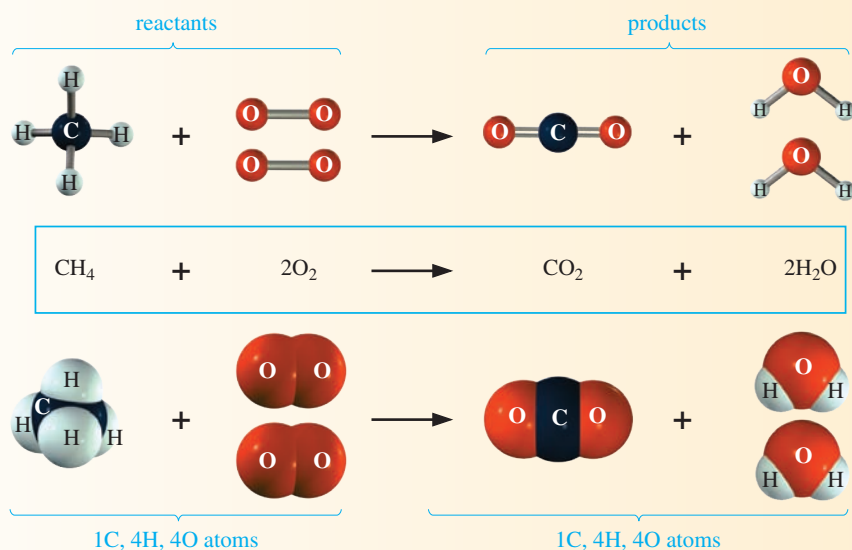
Chemical Equations and Reaction Stoichiometry

3



OUTLINE

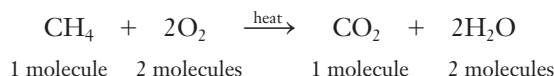
- 3-1 Chemical Equations
- 3-2 Calculations Based on Chemical Equations
- 3-3 The Limiting Reactant (Reagent) Concept
- 3-4 Percent Yields from Chemical Reactions
- 3-5 Sequential Reactions
- 3-6 Concentrations of Solutions
- 3-7 Dilution of Solutions
- 3-8 Using Solutions in Chemical Reactions



The combustion (burning) of methane (CH_4) with oxygen (O_2) produces mainly carbon dioxide (CO_2) and water (H_2O). Methane is the main component of natural gas.

Charles D. Winters

How do we interpret this equation? In the simplest terms, it tells us that methane reacts with oxygen to produce carbon dioxide, CO₂, and water. More specifically, it says that for every CH₄ molecule that reacts, two molecules of O₂ also react, and that one CO₂ molecule and two H₂O molecules are formed. That is,



► The arrow may be read “yields.” The capital Greek letter delta (Δ) is often used in place of the word “heat.”

This description of the reaction of CH₄ with O₂ is based on *experimental observations*. Many experiments have shown that when one CH₄ molecule reacts with two O₂ molecules, one CO₂ molecule and two H₂O molecules are formed. *Chemical equations are based on experimental observations*. Special conditions required for some reactions are indicated by a notation above or below the arrow. Figure 3-1 is a pictorial representation of the rearrangement of atoms described by this equation.

In Section 1-1, we learned the **Law of Conservation of Matter**: *there is no detectable change in the quantity of matter during an ordinary chemical reaction*. This guiding principle is the basis for “balancing” chemical equations and for performing calculations based on those equations. Because matter is neither created nor destroyed during a chemical reaction,

a balanced chemical equation must always include the same number of each kind of atom on both sides of the equation.

Chemists usually write equations with the smallest possible whole-number coefficients.

Before we attempt to balance an equation, all substances must be represented by formulas that describe them *as they exist*. For instance, we must write H₂ to represent diatomic hydrogen molecules—not H, which represents individual hydrogen atoms, which are unstable and do not exist by themselves under normal conditions. Once the correct formulas are written, the subscripts in the formulas may not be changed. Different subscripts in formulas specify different substances, so changing the formulas would mean that the equation would no longer describe the same reaction.

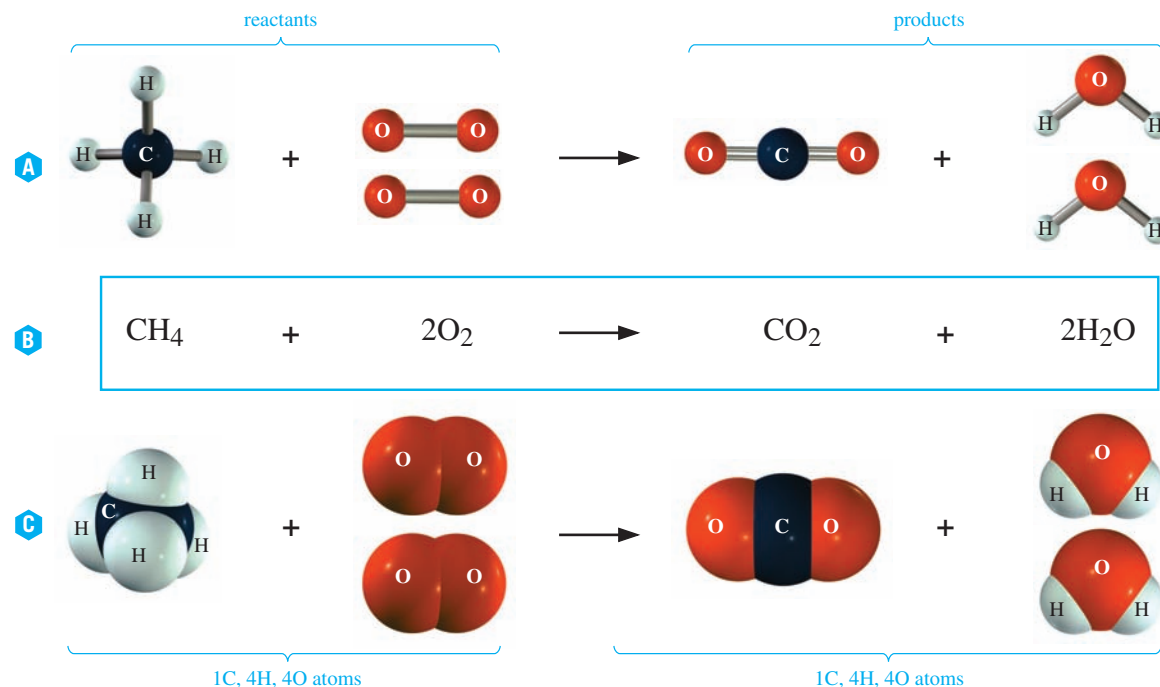


Figure 3-1 Three representations of the reaction of methane with oxygen to form carbon dioxide and water. Chemical bonds are broken and new ones are formed in each representation. Part (a) illustrates the reaction using ball-and-stick models, (b) uses chemical formulas, and (c) uses space-filling models.

Unless otherwise noted, all content on this page is © Cengage Learning.

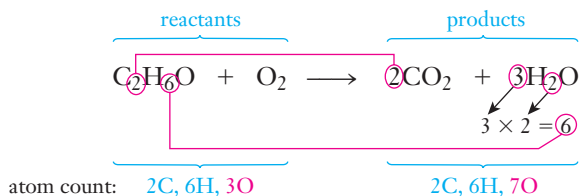
Dimethyl ether, $\text{C}_2\text{H}_6\text{O}$, burns in an excess of oxygen to give carbon dioxide and water. Let's balance the equation for this reaction. In unbalanced form, the equation is



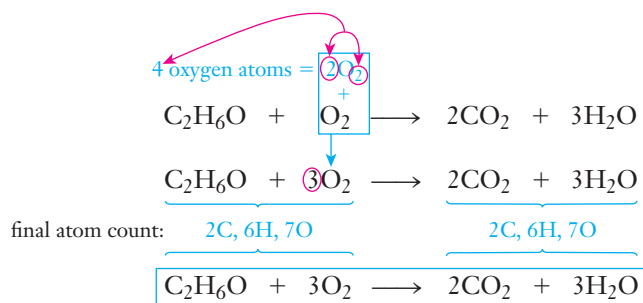
Carbon appears in only one compound on each side, and the same is true for hydrogen. We begin by balancing these elements. The subscripts on the carbon and hydrogen atoms in $\text{C}_2\text{H}_6\text{O}$ guide us in assigning the coefficients on the product side:

STOP & THINK

Remember to multiply all the atoms in a compound—including the subscript numbers—by the coefficient. But *do not* change the formulas of the elements or compounds; this would be changing the substances involved in the reaction!



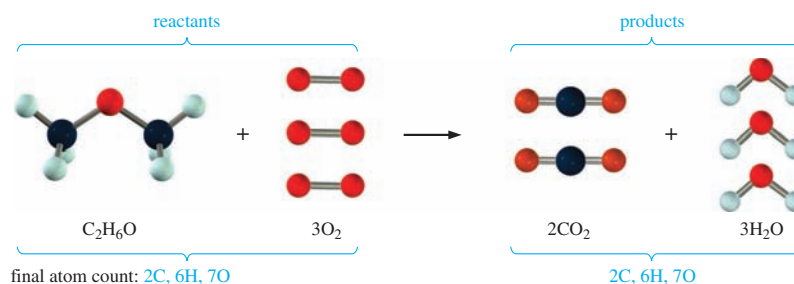
Now we have a different total number of O atoms on each side: 3 on the reactant side and 7 on the product side. We now need to balance the oxygen count by adding 4 more oxygen atoms to the reactant side. This is done by adding 2 more O_2 molecules (total of 4 oxygen atoms) to the one already present giving a total of 3 O_2 molecules on the reactant side:



STOP & THINK

Neglecting the final atom check to see if the equation is *really* balanced is a very common mistake. Remember to multiply the coefficient times the subscripts in a compound formula in order to count correctly all the atoms present!

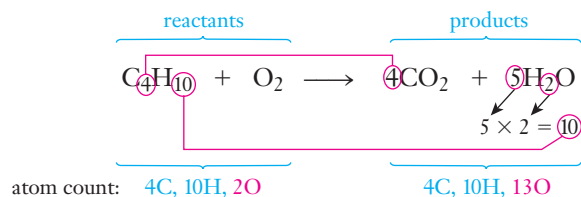
When we think we have finished the balancing, we should *always* do a complete check that the total number of atoms for each of the elements on the reactant side matches that found on the product side of the equation. A molecular view of this balanced equation using ball-and-stick models is shown next (element color coding: black = C, red = O, white = H).



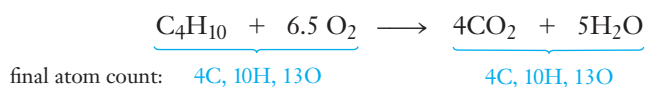
Let's examine a reaction that produces a fractional coefficient. Butane, C_4H_{10} , is used in many lighters. The combustion reaction with O_2 is initially written in unbalanced form as:



Once again, carbon only appears in one compound on each side and the same is true for hydrogen. We begin by balancing these elements. The subscripts on the carbon and hydrogen atoms in C_4H_{10} guide us in assigning the coefficients on the product side:

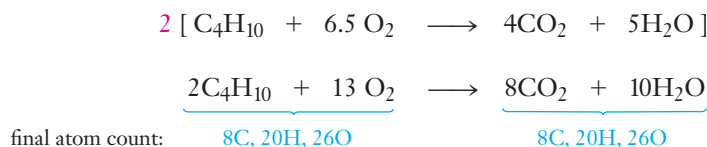


There are different total numbers of O atoms on each side: 2 on the reactant and 13 on the product side. We need to balance the oxygen count by adding 11 oxygen atoms to the reactant side. This is done by adding $1\frac{1}{2} = 5.5$ O_2 molecules to the one that is currently there, giving a total of $6\frac{1}{2}$ or 6.5 O_2 molecules on the reactant side:

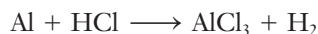


► If you are going to express a coefficient as a fractional value it is best to list it as a decimal number, e.g., 6.5 instead of $6\frac{1}{2}$ or $13/2$.

Although this is considered a properly balanced equation, many chemists do not ordinarily use fractional coefficients in chemical equations. To convert the fractional coefficient into an integer value, one simply multiplies the entire balanced equation by the proper integer value to convert the fractional value into the smallest integer value. In this case, one would multiply the entire equation by a factor of 2 to produce the final balanced equation with all integer coefficients:

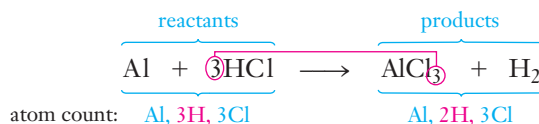


Let's generate the balanced equation for the reaction of aluminum metal with hydrogen chloride to produce aluminum chloride and hydrogen. The unbalanced "equation" is

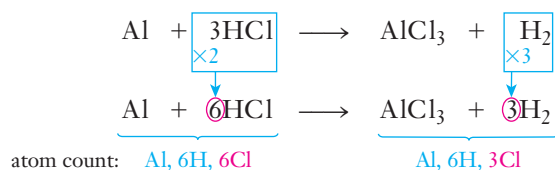


As it now stands, the "equation" does not satisfy the Law of Conservation of Matter because there are two H atoms in the H_2 molecule and three Cl atoms in one formula unit of AlCl_3 (product side), but only one H atom and one Cl atom in the HCl molecule (reactant side).

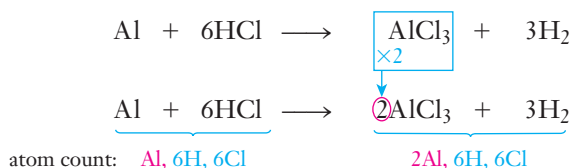
Let's first balance chlorine by putting a coefficient of 3 in front of HCl.



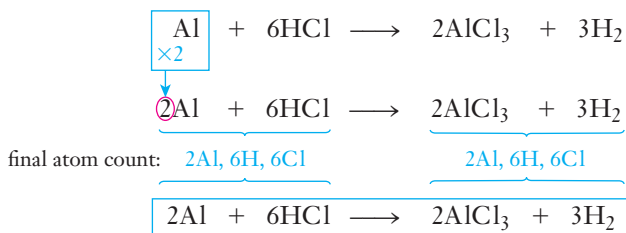
Now there are 3H on the left and 2H on the right. We can add hydrogen only as two atoms at a time (as H_2) on the product side. So we need to find the least common multiple of 3 and 2, which is 6, in order to balance the H atoms. To get a total of 6H atoms on each side, we multiply the 3HCl by 2 and the lone H_2 by 3. This now gives



Now Cl is again unbalanced (6Cl on the left, 3Cl on the right), but we can fix this by putting a coefficient of 2 in front of AlCl_3 on the product side.



Now all elements except Al are balanced (1Al on the left, 2Al on the right); we complete the balancing by putting a coefficient of 2 in front of Al on the reactant side.



► Note the iterative nature of this balancing process. It is important to keep track of the total reactant and product atom counts to help decide which material to balance next.

Balancing chemical equations “by inspection” is a *trial-and-error* approach. It requires a great deal of practice, but it is *very important*! Remember that we use the smallest whole-number coefficients. Some chemical equations are difficult to balance by inspection or “trial and error.” In Chapter 11 we will learn methods for balancing complex equations.

Problem-Solving Tip Balancing Chemical Equations

There is no one best place to start when balancing a chemical equation, but the following suggestions might be helpful:

1. Look for elements that appear in only one place on each side of the equation (in only one reactant and in only one product), and balance those elements first.
2. A good starting point is usually to pick a pair of compounds with a common element. Then focus on the compound with the largest subscript for the element in question to see if you can use that subscript as the coefficient for the other compound.
3. If free, uncombined elements appear on either side, balance them last.

Notice how these suggestions worked in the procedures illustrated in this section. Above all, remember that we should *never* change subscripts in formulas, because doing so would describe different substances. We adjust only the coefficients to balance the equation.

EXAMPLE 3-1 Balancing Chemical Equations



Balance the following chemical equations:

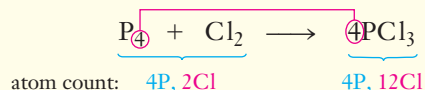
- (a) $\text{P}_4 + \text{Cl}_2 \longrightarrow \text{PCl}_3$
- (b) $\text{RbOH} + \text{SO}_2 \longrightarrow \text{Rb}_2\text{SO}_3 + \text{H}_2\text{O}$
- (c) $\text{P}_4\text{O}_{10} + \text{Ca}(\text{OH})_2 \longrightarrow \text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O}$

Plan

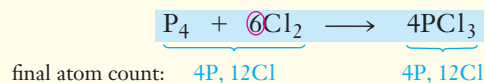
For each equation, we balance one element at a time by inspection, making sure that there are the same numbers of each type of element on the reactant and product sides of the equations.

Solution

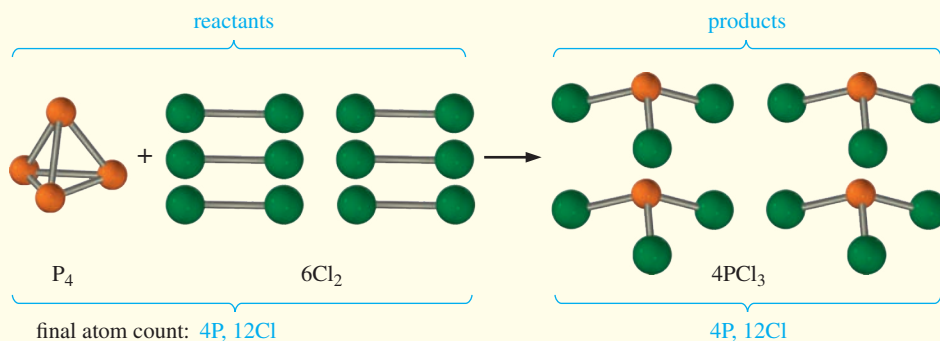
(a) Let's first balance P.



Now we need 10 more Cl atoms on the reactant side. But Cl_2 comes in increments of 2Cl atoms, so we need 5 *more* Cl_2 molecules, or a total of 6 Cl_2 :

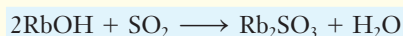


A molecular view of this balanced reaction using ball-and-stick models is shown next (element color coding: orange = P, green = Cl).



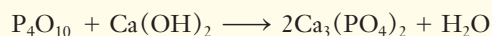
As a check, we see that there are 4P and 12Cl on each side, so the equation is balanced.

(b) We can first balance Rb.



We see that each side now has 2Rb, 1S, 2H, and 4O, so the equation is balanced.

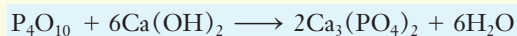
(c) Let's balance P first. There are two P on the right and 4P on the left, so we multiply $\text{Ca}_3(\text{PO}_4)_2$ by 2.



Next we can balance Ca by multiplying $\text{Ca}(\text{OH})_2$ by 6.

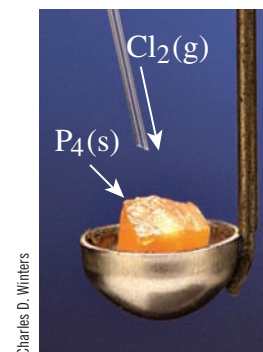


Now we see that there are 12H on the left and only 2H on the right, so we multiply H_2O by 6.



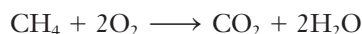
Checking the O balance we see that there are $(10 + (2 \times 6)) = 22\text{O}$ on the left and $((2 \times 4 \times 2) + (6 \times 1)) = 22\text{O}$ on the right. All other elements are also balanced so the equation is balanced.

You should now work Exercises 8 and 10.

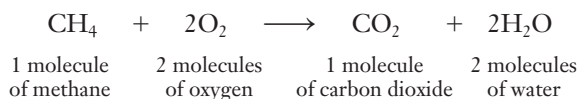


3-2 Calculations Based on Chemical Equations

We are now ready to use chemical equations to calculate the relative *amounts* of substances involved in chemical reactions. Let us again consider the combustion of methane in oxygen. The balanced chemical equation for that reaction is



On a quantitative basis, at the molecular level, the equation says



EXAMPLE 3-2 Number of Molecules



How many O_2 molecules react with 47 CH_4 molecules according to the preceding equation?

Plan

The *balanced* equation tells us that *one* CH_4 molecule reacts with *two* O_2 molecules. We can construct two unit factors from this fact:

$$\frac{1 \text{ CH}_4 \text{ molecule}}{2 \text{ O}_2 \text{ molecules}} \quad \text{and} \quad \frac{2 \text{ O}_2 \text{ molecules}}{1 \text{ CH}_4 \text{ molecule}}$$

These expressions are unit factors for *this* reaction because the numerator and denominator are *chemically equivalent*. In other words, the numerator and the denominator represent the same amount of reaction. To convert CH_4 molecules to O_2 molecules, we multiply by the second of the two factors.

Solution

$$\text{? O}_2 \text{ molecules} = 47 \text{ CH}_4 \text{ molecules} \times \frac{\overset{\text{reaction ratio from balanced equation}}{2 \text{ O}_2 \text{ molecules}}}{1 \text{ CH}_4 \text{ molecule}} = 94 \text{ O}_2 \text{ molecules}$$

You should now work Exercise 12.

► A balanced chemical equation may be interpreted on a *molecular* basis.

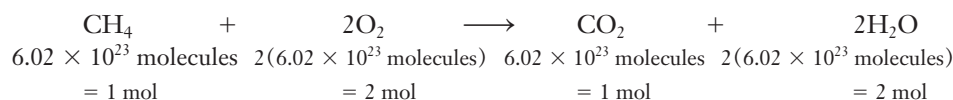
STOP & THINK

The balanced equation shows two O_2 molecules and only one CH_4 molecule, so it is reasonable that the number of O_2 molecules that react is twice the number of CH_4 molecules that react.

► We usually cannot work with individual molecules; a mole of a substance is an amount we might use in a laboratory experiment.

► A balanced chemical equation may be interpreted in terms of *moles* of reactants and products.

A chemical equation also indicates the relative amounts of each reactant and product in a given chemical reaction. We showed earlier that formulas can represent moles of substances. Suppose Avogadro's number of CH_4 molecules, rather than just one CH_4 molecule, undergo this reaction. Then the equation can be written



This interpretation tells us that *one* mole of methane reacts with *two* moles of oxygen to produce *one* mole of carbon dioxide and *two* moles of water.

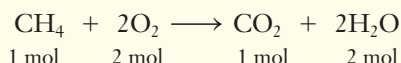
EXAMPLE 3-3 Number of Moles Formed



How many moles of water could be produced by the reaction of 3.5 moles of methane with excess oxygen (i.e., more than a sufficient amount of oxygen is present)?

Plan

The equation for the combustion of methane



► Please don't try to memorize unit factors for chemical reactions; instead, learn the general *method* for constructing them from balanced chemical equations.

Unless otherwise noted, all content on this page is © Cengage Learning.

shows that 1 mol of methane reacts with 2 mol of oxygen to produce 2 mol of water. From this information we construct two *unit factors*:

$$\frac{1 \text{ mol CH}_4}{2 \text{ mol H}_2\text{O}} \quad \text{and} \quad \frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol CH}_4}$$

We use the second factor in this calculation.

Solution

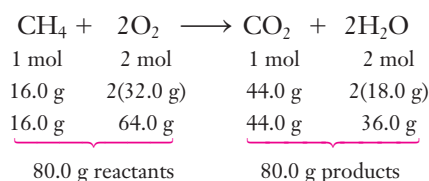
$$\underline{\hspace{1cm}} \text{ mol H}_2\text{O} = 3.5 \text{ mol CH}_4 \times \frac{\overset{\text{reaction ratio from}}{\underset{\text{balanced equation}}{2 \text{ mol H}_2\text{O}}}}{1 \text{ mol CH}_4} = 7.0 \text{ mol H}_2\text{O}$$

You should now work Exercises 14 and 18.

STOP & THINK

The balanced equation shows 2 moles of H₂O and only 1 mole of CH₄, so it is reasonable that the number of moles of H₂O produced is twice the number of moles of CH₄ that react.

We know the mass of 1 mol of each of these substances, so we can also write



The equation now tells us that 16.0 g of CH₄ reacts with 64.0 g of O₂ to form 44.0 g of CO₂ and 36.0 g of H₂O. The Law of Conservation of Matter is satisfied. Chemical equations describe **reaction ratios**, that is, the *mole ratios* of reactants and products as well as the *mass ratios* of reactants and products.

► A balanced equation may be interpreted on a *mass* basis.



Problem-Solving Tip Use the Reaction Ratio in Calculations with Balanced Chemical Equations

The most important way of interpreting the balanced chemical equation is in terms of moles. We use the coefficients to find the reaction ratio (in moles) of any two substances we want to relate. Then we apply it as

$$\frac{\text{moles of}}{\text{substance}} = \left(\frac{\text{moles of}}{\text{substance}} \right) \times \left(\frac{\text{reaction ratio}}{\text{from balanced}} \right)$$

It is important to include the substance formulas as part of the units; this can help us decide how to set up the unit factors. Notice that in Example 3-3 we want to cancel the term mol CH₄, so we know that mol CH₄ must be in the denominator of the mole ratio by which we multiply; we want mol H₂O as the answer, so mol H₂O must appear

in the numerator of the mole ratio. In other words, do not just write $\frac{\text{mol}}{\text{mol}}$; write

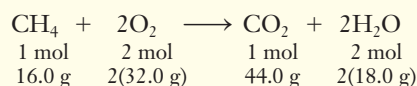
$\frac{\text{mol of something}}{\text{mol of something else}}$, giving the formulas of the two substances involved.

EXAMPLE 3-4 Mass of a Reactant Required

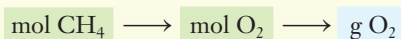
What mass of oxygen is required to react completely with 1.20 moles of CH₄?

Plan

The balanced equation



gives the relationships among moles and grams of reactants and products.



Solution

$$\underline{\hspace{1cm}} \text{ g O}_2 = 1.20 \text{ mol CH}_4 \times \overset{\text{reaction ratio from balanced equation}}{\frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4}} \times \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} = 76.8 \text{ g O}_2$$

STOP & THINK

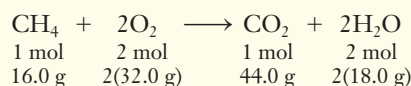
Remember to use the proper coefficient from the balanced equation to set up this reaction ratio expression.

EXAMPLE 3-5 Mass of a Reactant Required

What mass of oxygen is required to react completely with 24.0 g of CH₄?

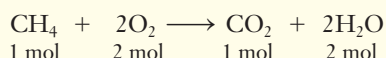
Plan

Recall the balanced equation in Example 3-4.



This shows that 1 mol of CH₄ reacts with 2 mol of O₂. These two quantities are chemically equivalent, so we can construct *unit factors*.

Solution



$$\begin{aligned} \underline{\hspace{1cm}} \text{ mol CH}_4 &= 24.0 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} = 1.50 \text{ mol CH}_4 \\ \underline{\hspace{1cm}} \text{ mol O}_2 &= 1.50 \text{ mol CH}_4 \times \frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4} = 3.00 \text{ mol O}_2 \\ \underline{\hspace{1cm}} \text{ g O}_2 &= 3.00 \text{ mol O}_2 \times \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} = 96.0 \text{ g O}_2 \end{aligned}$$

All these steps could be combined into one setup in which we convert



$$\underline{\hspace{1cm}} \text{ g O}_2 = 24.0 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} \times \frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4} \times \frac{32.0 \text{ g O}_2}{1 \text{ mol O}_2} = 96.0 \text{ g O}_2$$

The same answer, 96.0 g of O₂, is obtained by both methods.

You should now work Exercise 22.

STOP & THINK

The balanced equation shows more moles of O₂ than of CH₄; furthermore, a mole of O₂ has a greater mass (32.0 g) than a mole of CH₄ (16.0 g). Thus it is reasonable that the mass of O₂ that reacts is considerably greater than the mass of CH₄.

STOP & THINK

When a problem such as this gives the amount of a substance in grams, you almost always have to convert it to moles as the first step. These unit factors are the reciprocals of those used in Example 3-5.

The question posed in Example 3-5 may be reversed, as in Example 3-6.

EXAMPLE 3-6 Mass of a Reactant Required

What mass of CH₄, in grams, is required to react with 96.0 g of O₂?

Plan

We recall that 1 mole of CH₄ reacts with 2 moles of O₂.

Solution

$$\underline{\hspace{1cm}} \text{ g CH}_4 = 96.0 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \times \frac{1 \text{ mol CH}_4}{2 \text{ mol O}_2} \times \frac{16.0 \text{ g CH}_4}{1 \text{ mol CH}_4} = 24.0 \text{ g CH}_4$$

You should now work Exercise 24.

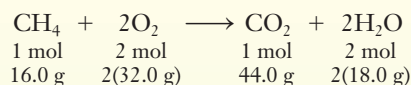
This is the amount of CH₄ in Example 3-5 that reacted with 96.0 g of O₂.

EXAMPLE 3-7 Mass of a Product Formed

Most combustion reactions occur in excess O_2 , that is, more than enough O_2 to burn the substance completely. Calculate the mass of CO_2 , in grams, that can be produced by burning 6.00 moles of CH_4 in excess O_2 .

Plan

The balanced equation tells us that 1 mole of CH_4 produces 1 mole of CO_2 .

**Solution**

$$\underline{\hspace{1cm}} \text{ g } CO_2 = 6.00 \text{ mol } CH_4 \times \overbrace{\frac{1 \text{ mol } CO_2}{1 \text{ mol } CH_4}}^{\text{reaction ratio from balanced equation}} \times \frac{44.0 \text{ g } CO_2}{1 \text{ mol } CO_2} = 2.64 \times 10^2 \text{ g } CO_2$$

You should now work Exercise 26.

► It is important to recognize that the reaction must stop when the 6.00 moles of CH_4 has been used up. Some O_2 will remain unreacted.

STOP & THINK

Note that even though there is excess O_2 present, we still use the balanced chemical equation to solve the problem.

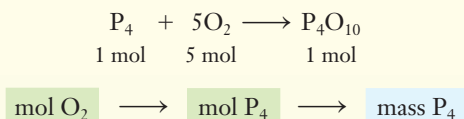
Reaction stoichiometry usually involves interpreting a balanced chemical equation to relate a *given* bit of information to the *desired* bit of information.

EXAMPLE 3-8 Mass of a Reactant Required

Phosphorus, P_4 , burns with excess oxygen to form tetraphosphorus decoxide, P_4O_{10} . In this reaction, what mass of P_4 reacts with 1.50 moles of O_2 ?

Plan

The balanced equation tells us that 1 mole of P_4 reacts with 5 moles of O_2 .

**Solution**

$$\underline{\hspace{1cm}} \text{ g } P_4 = 1.50 \text{ mol } O_2 \times \overbrace{\frac{1 \text{ mol } P_4}{5 \text{ mol } O_2}}^{\text{reaction ratio from balanced equation}} \times \frac{124.0 \text{ g } P_4}{1 \text{ mol } P_4} = 37.2 \text{ g } P_4$$

You should now work Exercise 28.

STOP & THINK

Never start a calculation involving a chemical reaction without first checking that the equation is balanced.

The possibilities for this kind of problem solving are limitless. Exercises 12–29 at the end of the chapter will give you important practice with such calculations.

3-3 The Limiting Reactant (Reagent) Concept

In the problems we have worked thus far, the presence of an excess of one reactant was stated or implied. The calculations were based on the substance that was used up first, called the **limiting reactant** or **reagent**. Before we study the concept of the limiting reactant in stoichiometry, let's develop the basic idea by considering a simple but analogous nonchemical example.

Suppose you have four slices of ham and six slices of bread and you wish to make as many ham sandwiches as possible using only one slice of ham and two slices of bread per sandwich. Obviously, you can make only three sandwiches, at which point you run out of bread. (In a chemical reaction this would correspond to one of the reactants being used

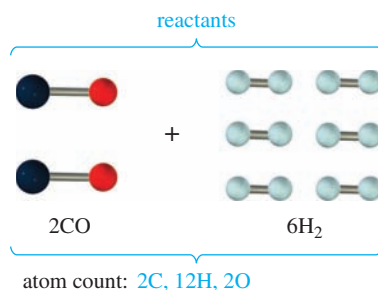
► Chemists often refer to the limiting reagent concept.

up—so the reaction would stop.) The bread is therefore the *limiting reactant*, and the extra slice of ham is the *excess reactant*. The amount of product, ham sandwiches, is determined by the amount of the limiting reactant, bread in this case. The limiting reactant is not necessarily the reactant present in the smallest amount. We have four slices of ham, the smallest amount, and six slices of bread, but the *reaction ratio* is two slices of bread to one piece of ham, so bread is the limiting reactant.

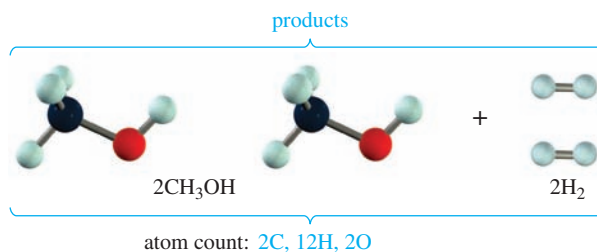
Consider the following balanced equation:



Suppose we have the following mixture shown here using ball-and-stick models (element color coding: black = C, red = O, white = H).



These can react to make only two molecules of CH₃OH (methanol), leaving two molecules of H₂ left over, as shown here.



In this example, H₂ molecules are present in excess (two more than needed to react with the CO molecules present). The other (and equal) way of looking at this reaction is that there are not enough CO molecules to react with all the H₂ molecules. The CO in this example is called the limiting reactant (chemists generally use the term *limiting reagent*).

The following examples show how the limiting reactant concept is applied to chemical calculations.

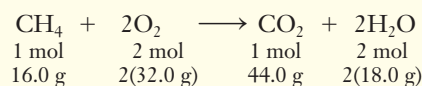
EXAMPLE 3-9 Limiting Reactant



What mass of CO₂ could be formed by the reaction of 16.0 g of CH₄ with 48.0 g of O₂?

Plan

The balanced equation tells us that 1 mole of CH₄ reacts with 2 moles of O₂.



We are given masses of both CH₄ and O₂, so we calculate the number of moles of each reactant, and then determine the number of moles of each reactant required to react with the other. From these calculations we identify the limiting reactant. Then we base the calculation on it.

STOP & THINK

Always remember to convert grams into moles for these types of problems! Then pay attention to the coefficients in the balanced chemical equation for guidance in determining the limiting reagent.

Solution

$$\underline{\hspace{1cm}} \text{ mol CH}_4 = 16.0 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} = \underline{1.00 \text{ mol CH}_4}$$

$$\underline{\hspace{1cm}} \text{ mol O}_2 = 48.0 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} = \underline{1.50 \text{ mol O}_2}$$

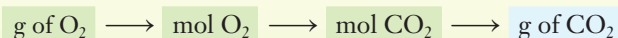
Now we return to the balanced equation. First we calculate the number of moles of O₂ that would be required to react with 1.00 mole of CH₄.

$$\underline{\hspace{1cm}} \text{ mol O}_2 = 1.00 \text{ mol CH}_4 \times \overbrace{\frac{2 \text{ mol O}_2}{1 \text{ mol CH}_4}}^{\text{reaction ratio from balanced equation}} = 2.00 \text{ mol O}_2$$

We see that 2.00 moles of O₂ are required, but we have only 1.50 moles of O₂, so O₂ is the limiting reactant. Alternatively, we can calculate the number of moles of CH₄ that would react with 1.50 moles of O₂.

$$\underline{\hspace{1cm}} \text{ mol CH}_4 = 1.50 \text{ mol O}_2 \times \frac{1 \text{ mol CH}_4}{2 \text{ mol O}_2} = 0.750 \text{ mol CH}_4$$

This tells us that only 0.750 mole of CH₄ would be required to react with 1.50 moles of O₂. But we have 1.00 mole of CH₄, so we see again that O₂ is the limiting reactant. The reaction must stop when the limiting reactant, O₂, is used up, so we base the calculation on O₂.



$$\underline{\hspace{1cm}} \text{ g CO}_2 = 48.0 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} \times \frac{1 \text{ mol CO}_2}{2 \text{ mol O}_2} \times \frac{44.0 \text{ g CO}_2}{1 \text{ mol CO}_2} = \underline{33.0 \text{ g CO}_2}$$

You should now work Exercise 30.

STOP & THINK

The chain of conversions gives the correct units (g CO₂).

Thus, 33.0 g of CO₂ is the most CO₂ that can be produced from 16.0 g of CH₄ and 48.0 g of O₂. If we had based our calculation simply on CH₄ rather than O₂, our answer would be too big (44.0 g) and *wrong* because more O₂ than we have would be required. This is why the limiting reagent concept is so important.

Another approach to problems like Example 3-9 is to calculate the number of moles of each reactant:

$$\underline{\hspace{1cm}} \text{ mol CH}_4 = 16.0 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} = \underline{1.00 \text{ mol CH}_4}$$

$$\underline{\hspace{1cm}} \text{ mol O}_2 = 48.0 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} = \underline{1.50 \text{ mol O}_2}$$

Then we return to the balanced equation. We first calculate the *required ratio* of reactants as indicated by the balanced chemical equation. We then calculate the *available ratio* of reactants and compare the two:

$$\begin{array}{l} \textbf{Required Ratio} \\ \frac{1 \text{ mol CH}_4}{2 \text{ mol O}_2} = \frac{0.500 \text{ mol CH}_4}{1.00 \text{ mol O}_2} \end{array}$$

$$\begin{array}{l} \textbf{Available Ratio} \\ \frac{1.00 \text{ mol CH}_4}{1.50 \text{ mol O}_2} = \frac{0.667 \text{ mol CH}_4}{1.00 \text{ mol O}_2} \end{array}$$

We see that each mole of O₂ requires exactly 0.500 mole of CH₄ to be completely used up. We have 0.667 mole of CH₄ for each mole of O₂, so there is more than enough CH₄ to react with the O₂ present. That means that there is *insufficient* O₂ to react with all the available CH₄. The reaction must stop when the O₂ is gone; O₂ is the limiting reactant, and we must base the calculation on it. (Suppose the available ratio of CH₄ to O₂ had been *smaller than* the required ratio. Then we would have concluded that there is not enough CH₄ to react with all the O₂, so CH₄ would have been the limiting reactant.)

Unless otherwise noted, all content on this page is © Cengage Learning.

Problem-Solving Tip Choosing the Limiting Reactant

Students often wonder how to know which ratio to calculate to help find the limiting reactant.

1. The ratio must involve the two reactants whose amounts are given in the problem.
2. It doesn't matter which way you calculate the ratios, as long as you calculate both required ratio and available ratio in the same order. For example, we could calculate the required and available ratios of $\frac{\text{mol O}_2}{\text{mol CH}_4}$ in the approach we just illustrated.
3. If you can't decide how to solve a limiting reactant problem, as a last resort you could do the entire calculation twice—once based on each reactant amount given. The *smaller* answer is the correct one.

STOP & THINK

When we are given the amounts of *two (or more)* reactants, we should suspect that we are dealing with a limiting reactant problem. It is very unlikely that *exactly* the stoichiometric amounts of both reactants are present in a reaction mixture.

► Even though the reaction occurs in aqueous solution, this calculation is similar to earlier examples because we are given the amounts of pure reactants.

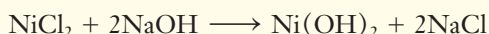


Charles Steele

A precipitate of solid $\text{Ni}(\text{OH})_2$ forms when colorless NaOH solution is added to green NiCl_2 solution. (Example 3-10.)

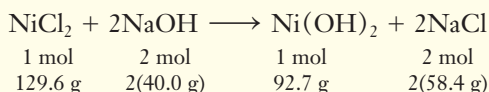
EXAMPLE 3-10 Limiting Reactant

What is the maximum mass of $\text{Ni}(\text{OH})_2$ that could be prepared by mixing two solutions that contain 25.9 g of NiCl_2 and 10.0 g of NaOH , respectively?



Plan

Interpreting the balanced equation as usual, we have



We determine the number of moles of NiCl_2 and NaOH present. Then we find the number of moles of each reactant required to react with the other reactant. These calculations identify the limiting reactant. We base the calculation on it.

Solution

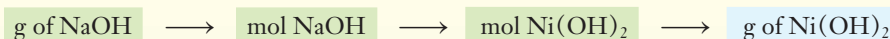
$$\underline{\hspace{1cm}} \text{ mol NiCl}_2 = 25.9 \text{ g NiCl}_2 \times \frac{1 \text{ mol NiCl}_2}{129.6 \text{ g NiCl}_2} = 0.200 \text{ mol NiCl}_2$$

$$\underline{\hspace{1cm}} \text{ mol NaOH} = 10.0 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.0 \text{ g NaOH}} = 0.250 \text{ mol NaOH}$$

We return to the balanced equation and calculate the number of moles of NaOH required to react with 0.200 mole of NiCl_2 .

$$\underline{\hspace{1cm}} \text{ mol NaOH} = 0.200 \text{ mol NiCl}_2 \times \frac{2 \text{ mol NaOH}}{1 \text{ mol NiCl}_2} = 0.400 \text{ mol NaOH}$$

But we have only 0.250 mole of NaOH , so NaOH is the limiting reactant.



$$\begin{aligned} \underline{\hspace{1cm}} \text{ g Ni}(\text{OH})_2 &= 10.0 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.0 \text{ g NaOH}} \times \overbrace{\frac{1 \text{ mol Ni}(\text{OH})_2}{2 \text{ mol NaOH}}}^{\text{reaction ratio from balanced equation}} \times \frac{92.7 \text{ g Ni}(\text{OH})_2}{1 \text{ mol Ni}(\text{OH})_2} \\ &= 11.6 \text{ g Ni}(\text{OH})_2 \end{aligned}$$

You should now work Exercises 34 and 36.

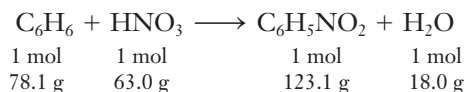
3-4 Percent Yields from Chemical Reactions

The **theoretical yield** from a chemical reaction is the yield calculated by assuming that the reaction goes to completion. In practice we often do not obtain as much product from a reaction mixture as is theoretically possible. There are several reasons for this. (1) Many reactions do not go to completion; that is, the reactants are not completely converted to products. (2) In some cases, a particular set of reactants undergoes two or more reactions simultaneously, forming undesired products as well as desired products. Reactions other than the desired one are called *side reactions*. (3) In some cases, separation of the desired product from the reaction mixture is so difficult that not all of the product formed is successfully isolated. The **actual** or **isolated yield** is the amount of a specified pure product actually obtained from a given reaction.

The term **percent yield** is used to indicate how much of a desired product is obtained from a reaction.

$$\text{percent yield} = \frac{\text{actual yield of product}}{\text{theoretical yield of product}} \times 100\%$$

Consider the preparation of nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, by the reaction of a limited amount of benzene, C_6H_6 , with excess nitric acid, HNO_3 . The balanced equation for the reaction may be written as



EXAMPLE 3-11 Percent Yield

A 15.6-g sample of C_6H_6 is mixed with excess HNO_3 . We isolate 18.0 g of $\text{C}_6\text{H}_5\text{NO}_2$. What is the percent yield of $\text{C}_6\text{H}_5\text{NO}_2$ in this reaction?

Plan

First we interpret the balanced chemical equation to calculate the theoretical yield of $\text{C}_6\text{H}_5\text{NO}_2$. Then we use the actual (isolated) yield and the previous definition to calculate the percent yield.

Solution

We calculate the theoretical yield of $\text{C}_6\text{H}_5\text{NO}_2$.

$$\begin{aligned} ? \text{ g C}_6\text{H}_5\text{NO}_2 &= 15.6 \text{ g C}_6\text{H}_6 \times \frac{1 \text{ mol C}_6\text{H}_6}{78.1 \text{ g C}_6\text{H}_6} \times \frac{\text{reaction ratio from balanced equation}}{1 \text{ mol C}_6\text{H}_6} \times \frac{123.1 \text{ g C}_6\text{H}_5\text{NO}_2}{1 \text{ mol C}_6\text{H}_5\text{NO}_2} \\ &= 24.6 \text{ g C}_6\text{H}_5\text{NO}_2 \leftarrow \text{theoretical yield} \end{aligned}$$

This tells us that if *all* the C_6H_6 were converted to $\text{C}_6\text{H}_5\text{NO}_2$ and isolated, we should obtain 24.6 g of $\text{C}_6\text{H}_5\text{NO}_2$ (100% yield). We isolate only 18.0 g of $\text{C}_6\text{H}_5\text{NO}_2$, however.

$$\text{percent yield} = \frac{\text{actual yield of product}}{\text{theoretical yield of product}} \times 100\% = \frac{18.0 \text{ g}}{24.6 \text{ g}} \times 100\% = 73.2\%$$

You should now work Exercise 44.

► In the examples we have worked to this point, the amounts of products that we calculated were theoretical yields.

► It is not necessary to know the mass of 1 mole of HNO_3 to solve this problem.

STOP & THINK
Percent yield can never exceed 100%, so this answer is reasonable.

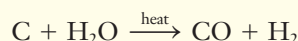
The amount of nitrobenzene obtained *in this experiment* is 73.2% of the amount that would be expected *if* the reaction had gone to completion, *if* there were no side reactions, and *if* we could have recovered all the product as a pure substance.

3-5 Sequential Reactions

Often more than one reaction is required to convert starting materials into the desired products. This is true for many reactions that we carry out in the laboratory and for many industrial processes. These are called **sequential reactions**. The amount of desired product from each reaction is taken as the starting material for the next reaction.

EXAMPLE 3-12 Sequential Reactions

At high temperatures, carbon reacts with water to produce a mixture of carbon monoxide, CO, and hydrogen, H₂.



Carbon monoxide is separated from H₂ and then used to separate nickel from cobalt by forming a gaseous compound, nickel tetracarbonyl, Ni(CO)₄.



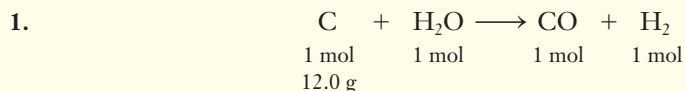
What mass of Ni(CO)₄ could be obtained from the CO produced by the reaction of 75.0 g of carbon? Assume 100% yield.

Plan

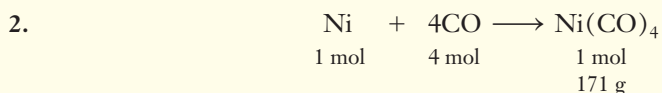
We interpret both chemical equations in the usual way, and solve the problem in two steps. They tell us that one mole of C produces one mole of CO and that four moles of CO is required to produce one mole of Ni(CO)₄.

1. We determine the number of moles of CO formed in the first reaction.
2. From the number of moles of CO produced in the first reaction, we calculate the number of grams of Ni(CO)₄ formed in the second reaction.

Solution

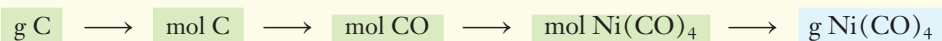


$$\underline{\hspace{1cm}} \text{ mol CO} = 75.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} \times \overbrace{\frac{1 \text{ mol CO}}{1 \text{ mol C}}}^{\text{reaction ratio from balanced equation}} = 6.25 \text{ mol CO}$$



$$\underline{\hspace{1cm}} \text{ g Ni}(\text{CO})_4 = 6.25 \text{ mol CO} \times \overbrace{\frac{1 \text{ mol Ni}(\text{CO})_4}{4 \text{ mol CO}}}^{\text{reaction ratio from balanced equation}} \times \frac{171 \text{ g Ni}(\text{CO})_4}{1 \text{ mol Ni}(\text{CO})_4} = 267 \text{ g Ni}(\text{CO})_4$$

Alternatively, we can set up a series of unit factors based on the conversions in the reaction sequence and solve the problem in one setup.



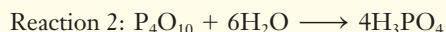
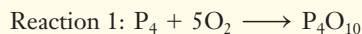
$$\begin{aligned} \underline{\hspace{1cm}} \text{ g Ni}(\text{CO})_4 &= 75.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} \times \overbrace{\frac{1 \text{ mol CO}}{1 \text{ mol C}} \times \frac{1 \text{ mol Ni}(\text{CO})_4}{4 \text{ mol CO}}}^{\text{reaction ratio from equations 1 \& 2}} \times \frac{171 \text{ g Ni}(\text{CO})_4}{1 \text{ mol Ni}(\text{CO})_4} \\ &= 267 \text{ g Ni}(\text{CO})_4 \end{aligned}$$

You should now work Exercise 50.

EXAMPLE 3-13 Sequential Reactions, Percent Yield

Phosphoric acid, H_3PO_4 , is a very important compound used to make fertilizers. It is also present in cola drinks.

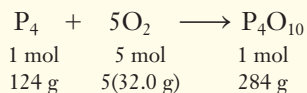
H_3PO_4 can be prepared in a two-step process.



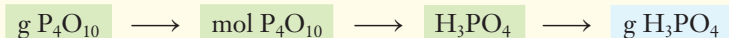
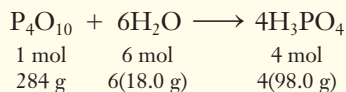
We allow 272 g of phosphorus to react with excess oxygen, which forms tetraphosphorus decoxide, P_4O_{10} , in 89.5% yield. In the second step reaction, a 96.8% yield of H_3PO_4 is obtained. What mass of H_3PO_4 is obtained?

Plan

1. We interpret the first equation as usual and calculate the amount of P_4O_{10} *obtained*.



2. Then we interpret the second equation and calculate the amount of H_3PO_4 *obtained* from the P_4O_{10} from the first step.

**Solution**

$$\begin{aligned} 1. \quad \underline{} \text{ g P}_4\text{O}_{10} &= 272 \text{ g P}_4 \times \frac{1 \text{ mol P}_4}{124 \text{ g P}_4} \times \frac{\text{reaction ratio from balanced equation}}{1 \text{ mol P}_4} \times \frac{284 \text{ g P}_4\text{O}_{10} \text{ theoretical}}{1 \text{ mol P}_4\text{O}_{10} \text{ theoretical}} \\ &\quad \times \left(\frac{89.5 \text{ g P}_4\text{O}_{10} \text{ actual}}{100 \text{ g P}_4\text{O}_{10} \text{ theoretical}} \right) = 558 \text{ g P}_4\text{O}_{10} \end{aligned}$$

$$\begin{aligned} 2. \quad \underline{} \text{ g H}_3\text{PO}_4 &= 558 \text{ g P}_4\text{O}_{10} \times \frac{1 \text{ mol P}_4\text{O}_{10}}{284 \text{ g P}_4\text{O}_{10}} \times \frac{4 \text{ mol H}_3\text{PO}_4}{1 \text{ mol P}_4\text{O}_{10}} \\ &\quad \times \frac{98.0 \text{ g H}_3\text{PO}_4 \text{ theoretical}}{1 \text{ mol H}_3\text{PO}_4 \text{ theoretical}} \times \left(\frac{96.8 \text{ g H}_3\text{PO}_4 \text{ actual}}{100 \text{ g H}_3\text{PO}_4 \text{ theoretical}} \right) = 746 \text{ g H}_3\text{PO}_4 \end{aligned}$$

You should now work Exercises 52 and 54.



Charles Steele

Two important uses for H_3PO_4 are in fertilizers and in cola drinks. Approximately 100 lb of H_3PO_4 -based fertilizer are used per person per year in America.

STOP & THINK

The unit factors that represent less than 100% reaction and/or less than 100% recovery are shown in parentheses. If you write “actual” and “theoretical” as part of the units, it will help you to generate the correct unit factors.

3-6 Concentrations of Solutions

Many chemical reactions are more conveniently carried out with the reactants mixed in solution rather than as pure substances. A **solution** is a homogeneous mixture, at the molecular level, of two or more substances. Simple solutions usually consist of one substance, the **solute**, dissolved in another substance, the **solvent**. For example, solutions of hydrochloric acid can be prepared by dissolving hydrogen chloride (HCl , a gas at room temperature and atmospheric pressure) in water. Solutions of sodium hydroxide are prepared by dissolving solid NaOH in water. The solutions used in the laboratory are usually liquids, and the solvent is often water. These are called **aqueous solutions**.

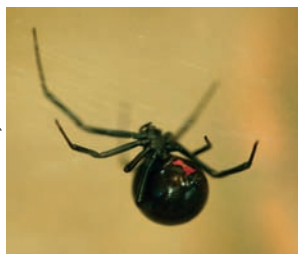
We often use solutions to supply the reactants for chemical reactions. Solutions allow intimate mixing of the reacting substances at the molecular level, much more than would be possible in solid form. (A practical example is drain cleaner, shown in the photo.) We

► For some solutions, such as a nearly equal mixture of ethyl alcohol and water, the distinction between *solute* and *solvent* is arbitrary.



Charles Steele

The sodium hydroxide and aluminum in some drain cleaners do not react while they are stored in solid form. When water is added, the NaOH dissolves and begins to act on trapped grease. At the same time, NaOH and Al react to produce H_2 gas; the resulting turbulence helps to dislodge the blockage. Do you see why the drain cleaner container should be kept tightly closed?



© David K. Werk/Alamy

A 10.0% solution of $Ca(C_6H_{11}O_7)_2$ is sometimes administered intravenously for emergency treatment of black widow spider bites.

STOP & THINK

The solution contains only a small percent $NiSO_4$, so it is reasonable that the total mass of solution must be much greater than the mass of $NiSO_4$.

sometimes adjust the concentrations of solutions to speed up or slow down the rate of a reaction. In this section we study methods for expressing the quantities of the various components present in a given amount of solution.

Concentrations of solutions are expressed in terms of *either* the amount of solute present in a given mass or volume of *solution*, *or* the amount of solute dissolved in a given mass or volume of *solvent*.

Percent by Mass

Concentrations of solutions may be expressed in terms of **percent by mass** of solute, which gives the mass of solute per 100 mass units of solution. The gram is the usual mass unit.

$$\text{percent solute} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

$$\text{percent solute} = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\%$$

Thus, a solution that is 10.0% calcium gluconate, $Ca(C_6H_{11}O_7)_2$, by mass contains 10.0 grams of calcium gluconate in 100.0 grams of *solution*. This could be described as 10.0 grams of calcium gluconate in 90.0 grams of water. The density of a 10.0% solution of calcium gluconate is 1.07 g/mL, so 100 mL of a 10.0% solution of calcium gluconate has a mass of 107 grams. Observe that 100 grams of a solution usually does *not* occupy 100 mL. Unless otherwise specified, percent means percent by *mass*, and water is the solvent.

EXAMPLE 3-14 Percent of Solute

Calculate the mass of nickel(II) sulfate, $NiSO_4$, contained in 200. g of a 6.00% solution of $NiSO_4$.

Plan

The percentage information tells us that the solution contains 6.00 g of $NiSO_4$ per 100. g of solution. The desired information is the mass of $NiSO_4$ in 200. g of solution. A unit factor is constructed by placing 6.00 g $NiSO_4$ over 100. g of solution. Multiplication of the mass of the solution, 200. g, by this unit factor gives the mass of $NiSO_4$ in the solution.

Solution

$$? \text{ g } NiSO_4 = 200. \text{ g soln} \times \frac{6.00 \text{ g } NiSO_4}{100. \text{ g soln}} = 12.0 \text{ g } NiSO_4$$

EXAMPLE 3-15 Mass of Solution

A 6.00% $NiSO_4$ solution contains 40.0 g of $NiSO_4$. Calculate the mass of the solution.

Plan

Placing 100. g of solution over 6.00 g of $NiSO_4$ gives the desired unit factor.

Solution

$$? \text{ g soln} = 40.0 \text{ g } NiSO_4 \times \frac{100. \text{ g soln}}{6.00 \text{ g } NiSO_4} = 667 \text{ g soln}$$

EXAMPLE 3-16 Mass of Solute

Calculate the mass of NiSO_4 present in 200. mL of a 6.00% solution of NiSO_4 . The density of the solution is 1.06 g/mL at 25°C.

Plan

The volume of a solution multiplied by its density gives the mass of the solution (see Section 1-12). The mass of the solution is then multiplied by the mass fraction due to NiSO_4 (6.00 g NiSO_4 /100. g soln) to give the mass of NiSO_4 in 200. mL of solution.

Solution

$$\begin{aligned} \text{? g NiSO}_4 &= 200. \text{ mL soln} \times \underbrace{\frac{1.06 \text{ g soln}}{1.00 \text{ mL soln}}}_{212 \text{ g soln}} \times \frac{6.00 \text{ g NiSO}_4}{100. \text{ g soln}} = 12.7 \text{ g NiSO}_4 \end{aligned}$$

You should now work Exercise 58.



Solid NiSO_4 and a 6% solution of NiSO_4 in water (Examples 3-14, 3-15, and 3-16).

EXAMPLE 3-17 Percent Solute and Density

What volume of a solution that is 15.0% iron(III) nitrate contains 30.0 g of $\text{Fe}(\text{NO}_3)_3$? The density of the solution is 1.16 g/mL at 25°C.

Plan

Two unit factors relate mass of $\text{Fe}(\text{NO}_3)_3$ and mass of solution, 15.0 g $\text{Fe}(\text{NO}_3)_3$ /100 g and 100 g/15.0 g $\text{Fe}(\text{NO}_3)_3$. The second factor converts grams of $\text{Fe}(\text{NO}_3)_3$ to grams of solution.

Solution

$$\begin{aligned} \text{? mL soln} &= 30.0 \text{ g Fe}(\text{NO}_3)_3 \times \underbrace{\frac{100 \text{ g soln}}{15.0 \text{ g Fe}(\text{NO}_3)_3}}_{200 \text{ g soln}} \times \frac{1.00 \text{ mL soln}}{1.16 \text{ g soln}} = 172 \text{ mL} \end{aligned}$$

Note that the answer is not 200. mL but considerably less because 1.00 mL of solution has a mass of 1.16 g; however, 172 mL of the solution has a mass of 200 g.

You should now work Exercise 60.

STOP & THINK

Write units “g of *what*” and “mL of *what*” to help you generate the correct unit factors. The solution is only a small percent $\text{Fe}(\text{NO}_3)_3$, so it is reasonable that the required mass of solution is considerably greater than the mass of $\text{Fe}(\text{NO}_3)_3$ it contains. The density (1.16 g/mL) tells us that each mL of solution has mass greater than 1 g, so the mL of solution required is numerically less than its mass in g.

Molarity

Molarity (M), or molar concentration, is a common unit for expressing the concentrations of solutions. **Molarity** is defined as the number of moles of solute per liter of solution:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}}$$

To prepare one liter of a one molar solution, one mole of solute is placed in a one-liter volumetric flask, enough solvent is added to dissolve the solute, and solvent is then added until the volume of the solution is exactly one liter. A 0.100 M solution contains 0.100 mole of solute per liter of solution, and a 0.0100 M solution contains 0.0100 mole of solute per liter of solution (Figure 3-2).

Water is the solvent in *most* of the solutions that we encounter. Unless otherwise indicated, we assume that water is the solvent. When the solvent is other than water, we state this explicitly.

STOP & THINK

Students sometimes make the mistake of assuming that one molar solution contains one mole of solute in a liter of solvent. This is not the case; one liter of solvent plus one mole of solute usually has a total volume of more than one liter.

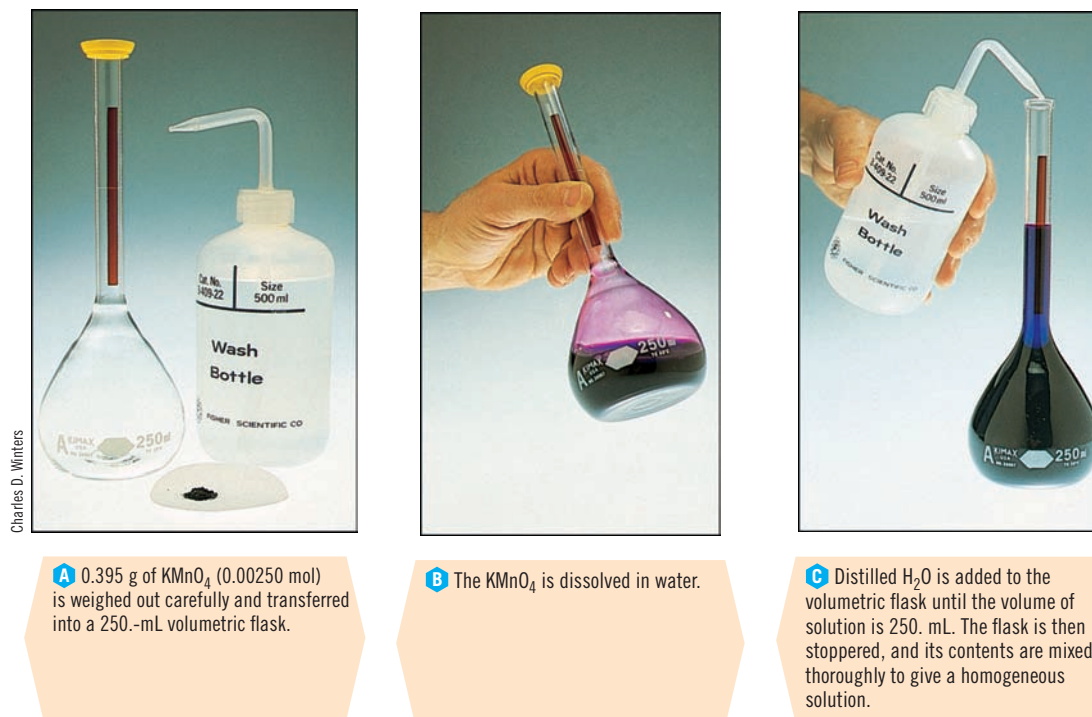


Figure 3-2 Preparation of 0.0100 *M* solution of KMnO_4 , potassium permanganate. A 250.-mL sample of 0.0100 *M* KMnO_4 solution contains 0.395 g of KMnO_4 (1 mol = 158 g).

EXAMPLE 3-18 Molarity

Calculate the molarity (*M*) of a solution that contains 3.65 g of HCl in 2.00 L of solution.

Plan

We are given the number of grams of HCl in 2.00 L of solution. We apply the definition of molarity, remembering to convert grams of HCl to moles of HCl.

Solution

$$\frac{? \text{ mol HCl}}{\text{L soln}} = \frac{3.65 \text{ g HCl}}{2.00 \text{ L soln}} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} = 0.0500 \text{ mol HCl/L soln}$$

The concentration of the HCl solution is 0.0500 molar, and the solution is called 0.0500 *M* hydrochloric acid. One liter of the solution contains 0.0500 mole of HCl.

You should now work Exercise 62.

► We place 3.65 g HCl over 2.00 L of solution, and then convert g HCl to mol HCl.

STOP & THINK

Remember to write explicit units. Moles of *what*? Grams of *what*? Although it takes more time, writing out the units and the substance formula (or name) will help you keep track of everything and minimize mistakes.

EXAMPLE 3-19 Mass of Solute

Calculate the mass of $\text{Ba}(\text{OH})_2$ required to prepare 2.50 L of a 0.0600 *M* solution of barium hydroxide.

Plan

The volume of the solution, 2.50 L, is multiplied by the concentration, 0.0600 mol $\text{Ba}(\text{OH})_2/\text{L}$, to give the number of moles of $\text{Ba}(\text{OH})_2$. The number of moles of $\text{Ba}(\text{OH})_2$ is then multiplied by the mass of $\text{Ba}(\text{OH})_2$ in one mole, 171.3 g $\text{Ba}(\text{OH})_2/\text{mol Ba}(\text{OH})_2$, to give the mass of $\text{Ba}(\text{OH})_2$ in the solution.

Solution

$$\frac{?}{1} \text{ g Ba(OH)}_2 = 2.50 \text{ L soln} \times \frac{0.0600 \text{ mol Ba(OH)}_2}{1 \text{ L soln}} \times \frac{171.3 \text{ g Ba(OH)}_2}{1 \text{ mol Ba(OH)}_2}$$

$$= 25.7 \text{ g Ba(OH)}_2$$

You should now work Exercise 64.

The solutions of acids and bases that are sold commercially are too concentrated for most laboratory uses. We often dilute these solutions before we use them. We must know the molar concentration of a stock solution before it is diluted. This can be calculated from the specific gravity and the percentage data given on the label of the bottle.

EXAMPLE 3-20 Molarity

A sample of commercial sulfuric acid is 96.4% H_2SO_4 by mass, and its specific gravity is 1.84. Calculate the molarity of this sulfuric acid solution.

Plan

The density of a solution, grams per milliliter, is numerically equal to its specific gravity, so the density of the solution is 1.84 g/mL. The solution is 96.4% H_2SO_4 by mass; therefore, 100. g of solution contains 96.4 g of pure H_2SO_4 . From this information, we can find the molarity of the solution. First, we calculate the mass of 1 L of solution.

Solution

$$\frac{?}{1} \frac{\text{g soln}}{\text{L soln}} = \frac{1.84 \text{ g soln}}{\text{mL soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} = 1.84 \times 10^3 \text{ g soln/L soln}$$

The solution is 96.4% H_2SO_4 by mass, so the mass of H_2SO_4 in 1 L is

$$\frac{?}{1} \frac{\text{g H}_2\text{SO}_4}{\text{L soln}} = \frac{1.84 \times 10^3 \text{ g soln}}{1 \text{ L soln}} \times \frac{96.4 \text{ g H}_2\text{SO}_4}{100. \text{ g soln}} = 1.77 \times 10^3 \text{ g H}_2\text{SO}_4/\text{L soln}$$

The molarity is the number of moles of H_2SO_4 per liter of solution.

$$\frac{?}{1} \frac{\text{mol H}_2\text{SO}_4}{\text{L soln}} = \frac{1.77 \times 10^3 \text{ g H}_2\text{SO}_4}{1 \text{ L soln}} \times \frac{1 \text{ mol H}_2\text{SO}_4}{98.1 \text{ g H}_2\text{SO}_4} = 18.0 \text{ mol H}_2\text{SO}_4/\text{L soln}$$

Thus, the solution is an 18.0 M H_2SO_4 solution. This problem can also be solved by using a series of three unit factors.

$$\frac{?}{1} \frac{\text{mol H}_2\text{SO}_4}{\text{L soln}} = \frac{1.84 \text{ g soln}}{\text{mL soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}} \times \frac{96.4 \text{ g H}_2\text{SO}_4}{100. \text{ g soln}} \times \frac{1 \text{ mol H}_2\text{SO}_4}{98.1 \text{ g H}_2\text{SO}_4}$$

$$= 18.1 \text{ mol H}_2\text{SO}_4/\text{L soln} = 18.1 \text{ M H}_2\text{SO}_4$$

You should now work Exercise 70.

ANALYSIS

Assay (H_2SO_4) W/W...Min. 95.0%—Max. 98.0%

MAXIMUM LIMITS OF IMPURITIES

Appearance.....	Passes A.C.S. Test
Color (APHA).....	10 Max.
Residue after Ignition.....	4 ppm
Chloride (Cl).....	0.2 ppm
Nitrate (NO_3).....	0.5 ppm
Ammonium (NH_4).....	1 ppm
Substances Reducing KMnO_4 (limit about 2ppm as SO_2).....	Passes A.C.S. Test
Arsenic (As).....	0.004 ppm
Heavy Metals (as Pb).....	0.8 ppm
Iron (Fe).....	0.2 ppm
Mercury (Hg).....	5 ppb
Specific Gravity.....	~1.84
Normality.....	~36

Suitable for Mercury Determinations

A label that shows the analysis of sulfuric acid.

STOP & THINK

Careful application of unit factors will help you solve this problem.

► The small difference between these two answers is due to rounding.

Problem-Solving Tip Write Complete Units

A common pitfall is to write units that are not complete enough to be helpful. For instance writing the density in Example 3-20 as just $\frac{1.84 \text{ g}}{\text{mL}}$ doesn't help us figure out the required

conversions. It is much safer to write $\frac{1.84 \text{ g soln}}{\text{mL soln}}$, $\frac{1000 \text{ mL soln}}{1 \text{ L soln}}$, $\frac{96.4 \text{ g H}_2\text{SO}_4}{100 \text{ g soln}}$, and so on. In Example 3-20, we have written complete units to help guide us through the problem.

3-7 Dilution of Solutions

Recall that the definition of molarity is the number of moles of solute divided by the volume of the solution in liters:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}}$$

Multiplying both sides of the equation by the volume, we obtain

$$\text{volume (in L)} \times \text{molarity} = \text{number of moles of solute}$$

Multiplication of the volume of a solution, in liters, by its molar concentration gives the amount of solute in the solution.

When we dilute a solution by mixing it with more solvent, the amount of solute present does not change. But the volume and the concentration of the solution *do* change. Because the same number of moles of solute is divided by a larger number of liters of solution, the molarity decreases. Using a subscript 1 to represent the original concentrated solution and a subscript 2 to represent the dilute solution, we obtain

$$\text{volume}_1 \times \text{molarity}_1 = \text{number of moles of solute} = \text{volume}_2 \times \text{molarity}_2$$

or

$$V_1M_1 = V_2M_2 \quad (\text{for dilution only})$$

This expression can be used to calculate any one of four quantities when the other three are known (Figure 3-3). We frequently need a certain volume of dilute solution of a given molarity for use in the laboratory, and we know the concentration of the initial solution available. Then we can calculate the amount of initial solution that must be used to make the dilute solution.



Water molecules not shown for clarity

A A 100.-mL volumetric flask is filled to the calibration line with a 0.100 M potassium chromate, K_2CrO_4 solution.

B Solution is transferred into a 1.00-L volumetric flask. The smaller flask is then rinsed three times with a small amount of distilled H_2O , which is also transferred into the larger flask.

C Distilled water is added to the 1.00-L flask until the liquid level coincides with its calibration line. The flask is stoppered and its contents are mixed thoroughly.

Figure 3-3 Dilution of a solution. The new solution is 0.0100 M K_2CrO_4 . (100. mL of 0.100 M K_2CrO_4 solution has been diluted to 1000. mL.) The 100. mL of original solution and the 1000. mL of final solution both contain the amount of K_2CrO_4 dissolved in the original 100. mL of 0.100 M K_2CrO_4 .

► A can of frozen orange juice contains a certain mass (or moles) of vitamin C. After the frozen contents of the can are diluted by addition of water, the amount of vitamin C in the resulting total amount of solution will be unchanged. The concentration, or amount per a selected volume, will be less in the final solution, however.

STOP & THINK

Never use this equation to relate two different substances in a chemical reaction. It applies only to dilution calculations.

► We could use any volume unit as long as we use the same unit on both sides of the equation. This relationship also applies when the concentration is changed by evaporating some solvent.

CAUTION!

Dilution of a concentrated solution, especially of a strong acid or base, frequently liberates a great deal of heat. This can vaporize drops of water as they hit the concentrated solution and can cause dangerous spattering. As a safety precaution, *concentrated solutions of acids or bases are always poured slowly into water*; allowing the heat to be absorbed by the larger quantity of water. Calculations are usually simpler to visualize, however, by assuming that the water is added to the concentrated solution.

EXAMPLE 3-21 Dilution

How many milliliters of 18.0 M H₂SO₄ are required to prepare 1.00 L of a 0.900 M solution of H₂SO₄?

Plan

The volume (1.00 L) and molarity (0.900 M) of the final solution and the molarity (18.0 M) of the original solution are given. We can use the relationship $V_1M_1 = V_2M_2$ with subscript 1 for the initial acid solution and subscript 2 for the dilute solution. We solve

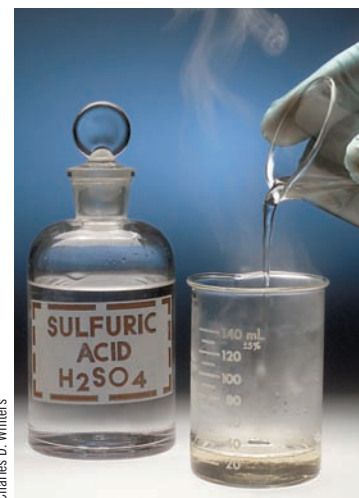
$$V_1M_1 = V_2M_2 \quad \text{for } V_1$$

Solution

$$V_1 = \frac{V_2M_2}{M_1} = \frac{1.00 \text{ L} \times 0.900 \text{ M}}{18.0 \text{ M}} = 0.0500 \text{ L} = 50.0 \text{ mL}$$

The dilute solution contains $1.00 \text{ L} \times 0.900 \text{ M} = 0.900$ mole of H₂SO₄, so 0.900 mole of H₂SO₄ must also be present in the original concentrated solution. Indeed, $0.0500 \text{ L} \times 18.0 \text{ M} = 0.900$ mole of H₂SO₄.

You should now work Exercises 72 and 74.



Charles D. Winters

Pouring concentrated H₂SO₄ into an equal volume of H₂O liberates a lot of heat—enough to raise the temperature of the resulting solution by as much as 100°C.

3-8 Using Solutions in Chemical Reactions

When we plan to carry out a reaction in a solution, we must calculate the amount of solution that we need. If we know the molarity of a solution, we can calculate the amount of solute contained in a specified volume of that solution. This procedure is illustrated in Example 3-22.

EXAMPLE 3-22 Amount of Solute

Calculate (a) the number of moles of H₂SO₄ and (b) the number of grams of H₂SO₄ in 500. mL of 0.324 M H₂SO₄ solution.

Plan

Because we have two parallel calculations in this example, we state the plan for each step just before the calculation is done.

Solution

- (a) The volume of a solution in liters multiplied by its molarity gives the number of moles of solute, H₂SO₄ in this case.

$$\underline{\hspace{1cm}} \text{ mol H}_2\text{SO}_4 = 0.500 \text{ L soln} \times \frac{\overbrace{0.324 \text{ mol H}_2\text{SO}_4}^{\text{molarity}}}{\text{L soln}} = 0.162 \text{ mol H}_2\text{SO}_4$$

- (b) We may use the results of part (a) to calculate the mass of H₂SO₄ in the solution.

$$\underline{\hspace{1cm}} \text{ g H}_2\text{SO}_4 = 0.162 \text{ mol H}_2\text{SO}_4 \times \frac{\overbrace{98.1 \text{ g H}_2\text{SO}_4}^{\text{ratio from formula weight}}}{1 \text{ mol H}_2\text{SO}_4} = 15.9 \text{ g H}_2\text{SO}_4$$

► 500. mL is more conveniently expressed as 0.500 L in this problem. By now, you should be able to convert mL to L (and the reverse) without writing out the conversion.

► A mole of H₂SO₄ is 98.1 g.

► Molarity can be used as a unit factor, that is, $\frac{\text{mol solute}}{\text{L soln}}$.

STOP & THINK

We have less than one liter of solution, and the molarity tells us that there is less than one mole in each liter of solution. Thus it is reasonable that (a) the number of moles of H_2SO_4 present is less than one, so (b) the mass of H_2SO_4 present is less than the formula weight (98.1 g/mol).

► Aqueous solutions (those in water) are indicated by (aq).

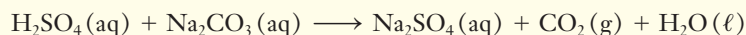
The mass of H_2SO_4 in the solution can be calculated without solving explicitly for the number of moles of H_2SO_4 .

$$\underline{\hspace{1cm}} \text{ g H}_2\text{SO}_4 = 0.500 \text{ L soln} \times \frac{0.324 \text{ mol H}_2\text{SO}_4}{\text{L soln}} \times \frac{98.1 \text{ g H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} = 15.9 \text{ g H}_2\text{SO}_4$$

One of the most important uses of molarity relates the volume of a solution of known concentration of one reactant to the mass of the other reactant.

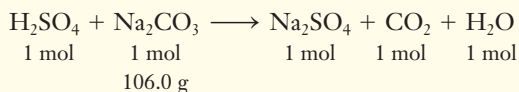
EXAMPLE 3-23 Solution Stoichiometry

Calculate the volume in liters and in milliliters of a 0.324 M solution of sulfuric acid required to react completely with 2.792 g of Na_2CO_3 according to the equation

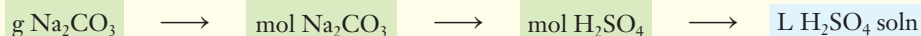


Plan

The balanced equation tells us that 1 mol H_2SO_4 reacts with 1 mol Na_2CO_3 , and we can write



We convert (1) grams of Na_2CO_3 to moles of Na_2CO_3 , (2) moles of Na_2CO_3 to moles of H_2SO_4 , and (3) moles of H_2SO_4 to liters of H_2SO_4 solution.

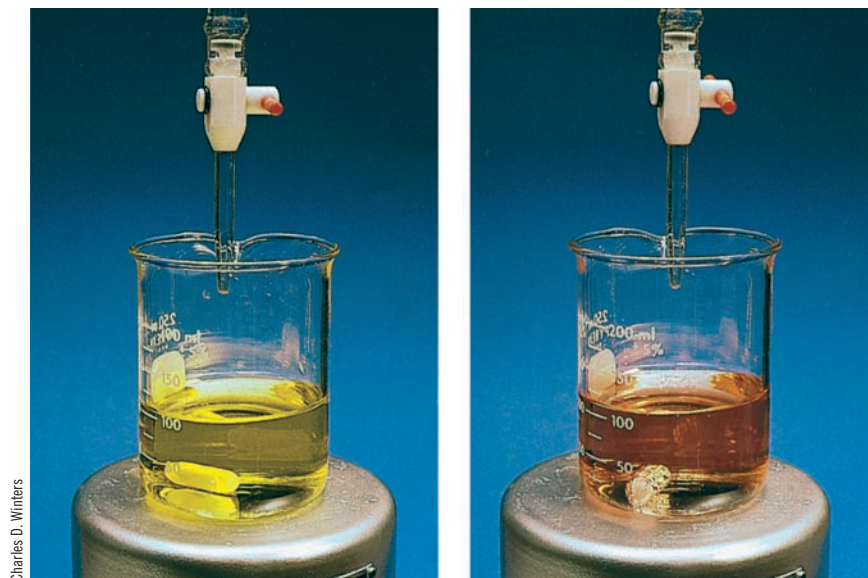


Solution

$$\begin{aligned} \underline{\hspace{1cm}} \text{ L H}_2\text{SO}_4 &= 2.792 \text{ g Na}_2\text{CO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{106.0 \text{ g Na}_2\text{CO}_3} \times \frac{1 \text{ mol H}_2\text{SO}_4}{1 \text{ mol Na}_2\text{CO}_3} \times \frac{1 \text{ L H}_2\text{SO}_4 \text{ soln}}{0.324 \text{ mol H}_2\text{SO}_4} \\ &= 0.0813 \text{ L H}_2\text{SO}_4 \text{ soln} \quad \text{or} \quad 81.3 \text{ mL H}_2\text{SO}_4 \text{ soln} \end{aligned}$$

You should now work Exercise 78.

► The indicator methyl orange changes from yellow, its color in basic solutions, to orange, its color in acidic solutions, when the reaction in Example 3-23 reaches completion.

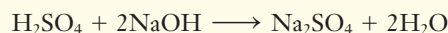


Unless otherwise noted, all content on this page is © Cengage Learning.

Often we must calculate the volume of a solution of known molarity that is required to react with a specified volume of another solution. We always examine the balanced chemical equation for the reaction to determine the *reaction ratio*, that is, the relative numbers of moles of reactants.

EXAMPLE 3-24 Volume of Solution Required

Find the volume in liters and in milliliters of a 0.505 M NaOH solution required to react with 40.0 mL of 0.505 M H₂SO₄ solution according to the reaction

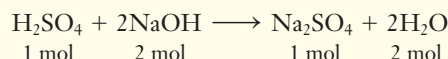


Plan

We shall work this example in several steps, stating the “plan,” or reasoning, just before each step in the calculation. Then we shall use a single setup to solve the problem.

Solution

The balanced equation tells us that the reaction ratio is 1 mol H₂SO₄ to 2 mol NaOH.



From the volume and the molarity of the H₂SO₄ solution, we can calculate the number of moles of H₂SO₄.

$$\text{? mol H}_2\text{SO}_4 = 0.0400 \text{ L H}_2\text{SO}_4 \text{ soln} \times \frac{\overbrace{0.505 \text{ mol H}_2\text{SO}_4}^{\text{molarity}}}{\text{L soln}} = 0.0202 \text{ mol H}_2\text{SO}_4$$

The number of moles of H₂SO₄ is related to the number of moles of NaOH by the reaction ratio, 1 mol H₂SO₄/2 mol NaOH:

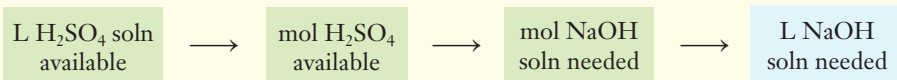
$$\text{? mol NaOH} = 0.0202 \text{ mol H}_2\text{SO}_4 \times \frac{\overbrace{2 \text{ mol NaOH}}^{\text{reaction ratio from balanced equation}}}{1 \text{ mol H}_2\text{SO}_4} = 0.0404 \text{ mol NaOH}$$

Now we can calculate the volume of 0.505 M NaOH solution that contains 0.0404 mole of NaOH:

$$\text{? L NaOH soln} = 0.0404 \text{ mol NaOH} \times \frac{\overbrace{1.00 \text{ L NaOH soln}}^{(\text{molarity})^{-1}}}{0.505 \text{ mol NaOH}} = 0.0800 \text{ L NaOH soln}$$

which we usually call 80.0 mL of NaOH solution.

We have worked through the problem stepwise; let us solve it in a single setup.



$$\begin{aligned} \text{? L NaOH soln} &= 0.0400 \text{ L H}_2\text{SO}_4 \text{ soln} \times \frac{0.505 \text{ mol H}_2\text{SO}_4}{\text{L H}_2\text{SO}_4 \text{ soln}} \times \frac{\overbrace{2 \text{ mol NaOH}}^{\text{reaction ratio from balanced equation}}}{1 \text{ mol H}_2\text{SO}_4} \\ &\quad \times \frac{1.00 \text{ L NaOH soln}}{0.505 \text{ mol NaOH}} \\ &= 0.0800 \text{ L NaOH soln or } 80.0 \text{ mL NaOH soln} \end{aligned}$$

You should now work Exercise 80.

STOP & THINK

A common mistake is to use the dilution equation $V_1M_1 = V_2M_2$ to solve problems involving reactions. Though it can sometimes give the correct answer, this is coincidental; for Example 3-24 it would give the wrong answer.

► The volume of H₂SO₄ solution is expressed as 0.0400 L rather than 40.0 mL.

► Again we see that molarity can be used as a unit factor. In this case,

$$\frac{1.00 \text{ L NaOH soln}}{0.505 \text{ mol NaOH}}$$

KEY TERMS

Actual yield The amount of a specified pure product actually obtained from a given reaction. Compare with *Theoretical yield*.

Aqueous solution A solution in which the solvent is water.

Chemical equation Description of a chemical reaction by placing the formulas of reactants on the left and the formulas of products on the right of an arrow. A chemical equation must be balanced; that is, it must have the same number of each kind of atom on both sides.

Concentration The amount of solute per unit volume or mass of solvent or of solution.

Dilution The process of reducing the concentration of a solute in solution, usually simply by adding more solvent.

Isolated yield see *Actual yield*.

Limiting reactant (or reagent) A substance that stoichiometrically limits the amount of product(s) that can be formed in a reaction.

Molarity (M) The number of moles of solute per liter of solution.

Percent by mass 100% multiplied by the mass of a solute divided by the mass of the solution in which it is contained.

Percent yield 100% times actual yield divided by theoretical yield.

Products Substances produced in a chemical reaction.

Reactants Substances consumed in a chemical reaction.

Reaction ratio The relative amounts of reactants and products involved in a reaction; may be the ratio of moles, or masses. Also called *Stoichiometric ratio*.

Reaction stoichiometry Description of the quantitative relationships among substances as they participate in chemical reactions.

Sequential reaction A chemical process in which several reaction steps are required to convert starting materials into products.

Solute The dispersed (dissolved) phase of a solution.

Solution A homogeneous mixture of two or more substances.

Solvent The dispersing medium of a solution.

Stoichiometric ratio see *Reaction ratio*.

Stoichiometry Description of the quantitative relationships among elements and compounds as they undergo chemical changes.

Theoretical yield The maximum amount of a specified product that could be obtained from specified amounts of reactants, assuming complete consumption of the limiting reactant according to only one reaction and complete recovery of the product. Compare with *Actual yield*.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Chemical Equations

- In a chemical equation, what are the products? What information must an unbalanced chemical equation contain?
- In a balanced chemical equation there must be the same number of atoms of each element on both sides of the equation. What scientific (natural) law requires that there be equal numbers of atoms of each element in both the products and the reactants?
- Write a balanced chemical equation for the following reaction. In sunlight hydrogen gas reacts explosively with chlorine gas to produce hydrogen chloride gas.
 - Use ball-and-stick models to illustrate the balanced chemical equation.
- Write a balanced chemical equation for the following reaction. In the presence of a spark, hydrogen gas reacts explosively with oxygen gas to produce gaseous water.
 - Use ball-and-stick models to illustrate the balanced chemical equation.
- Use words to state explicitly the relationships among numbers of molecules of reactants and products in the equation for the combustion of butane, C_4H_{10} .



A butane-fueled lighter

- Use words to state explicitly at the molecular level the information given in the following equation.

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$
- Write the chemical equation for the production of lithium oxide by the reaction of lithium and oxygen.

Balance each "equation" in Exercises 8-11 by inspection.

- $Na + O_2 \longrightarrow Na_2O$
 - $Mg_3N_2 + H_2O \longrightarrow NH_3 + Mg(OH)_2$
 - $LiCl + Pb(NO_3)_2 \longrightarrow PbCl_2 + LiNO_3$
 - $H_2O + KO_2 \longrightarrow KOH + O_2$
 - $H_2SO_4 + NH_3 \longrightarrow (NH_4)_2SO_4$

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

9. (a) $\text{Na} + \text{O}_2 \longrightarrow \text{Na}_2\text{O}_2$
 (b) $\text{P}_4 + \text{O}_2 \longrightarrow \text{P}_4\text{O}_{10}$
 (c) $\text{Ca}(\text{HCO}_3)_2 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + \text{NaHCO}_3$
 (d) $\text{NH}_3 + \text{O}_2 \longrightarrow \text{NO} + \text{H}_2\text{O}$
 (e) $\text{Rb} + \text{H}_2\text{O} \longrightarrow \text{RbOH} + \text{H}_2$
10. (a) $\text{Fe}_2\text{O}_3 + \text{CO} \longrightarrow \text{Fe} + \text{CO}_2$
 (b) $\text{Rb} + \text{H}_2\text{O} \longrightarrow \text{RbOH} + \text{H}_2$
 (c) $\text{K} + \text{KNO}_3 \longrightarrow \text{K}_2\text{O} + \text{N}_2$
 (d) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{H}_2\text{O} + \text{Cr}_2\text{O}_3$
 (e) $\text{Al} + \text{Cr}_2\text{O}_3 \longrightarrow \text{Al}_2\text{O}_3 + \text{Cr}$
11. (a) $\text{Al} + \text{H}_2\text{SO}_4 \longrightarrow \text{Al}_2(\text{SO}_4)_3 + \text{H}_2$
 (b) $\text{C}_5\text{H}_{10} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$
 (c) $\text{Li} + \text{N}_2 \longrightarrow \text{Li}_3\text{N}$
 (d) $\text{Ba}(\text{ClO}_4)_2 \longrightarrow \text{BaCl}_2 + \text{O}_2$
 (e) $\text{C}_2\text{H}_6\text{O} + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$
15. (a) Aluminum building materials have a hard, transparent, protective coating of aluminum oxide, Al_2O_3 , formed by reaction with oxygen in the air. The sulfuric acid, H_2SO_4 , in acid rain dissolves this protective coating and forms aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, and water.
 (b) How many moles of H_2SO_4 are required to react with 2.6 mol of Al_2O_3 ?
 (c) How many moles of $\text{Al}_2(\text{SO}_4)_3$ are formed in part (b)?
16. Calculate the number of grams of baking soda, NaHCO_3 , that contain 10.5 moles of carbon.



Charles D. Winters

Baking soda

Calculations Based on Chemical Equations

In Exercises 12–15, (a) write the balanced chemical equation that represents the reaction described by words, and then perform calculations to answer parts (b) and (c).

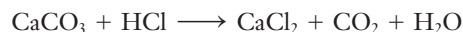
12. (a) Nitrogen, N_2 , combines with hydrogen, H_2 , to form ammonia, NH_3 .
 (b) How many hydrogen molecules are required to react with 150. nitrogen molecules?
 (c) How many ammonia molecules are formed in part (b)?
13. (a) Sulfur, S_8 , combines with oxygen at elevated temperatures to form sulfur dioxide.
 (b) If 160. oxygen molecules are used up in this reaction, how many sulfur molecules react?
 (c) How many sulfur dioxide molecules are formed in part (b)?
14. (a) Limestone, CaCO_3 , dissolves in hydrochloric acid, HCl , to form calcium chloride, CaCl_2 , carbon dioxide, and water.
 (b) How many moles of HCl are required to dissolve 2.6 mol of CaCO_3 ?
 (c) How many moles of water are formed in part (b)?



Charles D. Winters

Limestone dissolving in HCl

17. Limestone, coral, seashells, and marble are composed primarily of calcium carbonate. The test for the identification of a carbonate is to use a few drops of hydrochloric acid. The unbalanced equation is



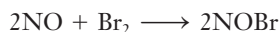
- (a) Balance the equation.
 (b) How many atoms are in 0.150 mol of calcium carbonate?
 (c) What number of carbon dioxide molecules is released by the reaction of 0.150 mol of calcium carbonate?
18. How many moles of oxygen can be obtained by the decomposition of 6.4 mol of reactant in each of the following reactions?
 (a) $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$
 (b) $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
 (c) $2\text{HgO} \longrightarrow 2\text{Hg} + \text{O}_2$
 (d) $2\text{NaNO}_3 \longrightarrow 2\text{NaNO}_2 + \text{O}_2$
 (e) $\text{KClO}_4 \longrightarrow \text{KCl} + 2\text{O}_2$
19. For the formation of 6.5 mol of water, which reaction uses the most nitric acid?
 (a) $3\text{Cu} + 8\text{HNO}_3 \longrightarrow 3\text{Cu}(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
 (b) $\text{Al}_2\text{O}_3 + 6\text{HNO}_3 \longrightarrow 2\text{Al}(\text{NO}_3)_3 + 3\text{H}_2\text{O}$
 (c) $4\text{Zn} + 10\text{HNO}_3 \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$
20. Consider the reaction



For every 6.40 mol of NH_3 , (a) how many moles of O_2 are required, (b) how many moles of NO are produced, and (c) how many moles of H_2O are produced?



21.  Consider the reaction



For every 6.25 mol of bromine that reacts, how many moles of (a) NO react and (b) NOBr are produced? (c) Represent the balanced equation with ball-and-stick models.

22. We allow 44.5 g of methane, CH_4 , to react as completely as possible with excess oxygen, O_2 , to form CO_2 and water. Write the balanced equation for this reaction. What mass of oxygen reacts?
23. Iron(III) oxide, Fe_2O_3 , is a result of the reaction of iron with the oxygen in air.
- What is the balanced equation for this reaction?
 - What number of moles of iron reacts with 15.25 mol of oxygen from the air?
 - What mass of iron is required to react with 15.25 mol of oxygen?
24. A sample of magnetic iron oxide, Fe_3O_4 , reacts completely with hydrogen at red heat. The water vapor formed by the reaction



is condensed and found to weigh 27.15 g. Calculate the mass of Fe_3O_4 that reacted.

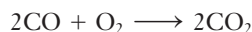
25. What masses of cobalt(II) chloride, CoCl_2 , and of hydrogen fluoride are needed to prepare 5.25 mol of cobalt(II) fluoride, CoF_2 , by the following reaction?
- $$\text{CoCl}_2 + 2\text{HF} \longrightarrow \text{CoF}_2 + 2\text{HCl}$$
26.  Sodium iodide, NaI , is a source of iodine used to produce iodized salt. (a) Write the balanced chemical equation for the reaction of sodium and iodine. (b) How many grams of sodium iodide are produced by the reaction of 47.24 grams of iodine?
27.  Calculate the mass of calcium required to react with 1.885 g of carbon during the production of calcium carbide, CaC_2 .
28. Calculate the mass of propane, C_3H_8 , that will produce 7.25 moles of water when burned in excess oxygen.



29. What mass of pentane, C_5H_{12} , produces 9.033×10^{22} CO_2 molecules when burned in excess oxygen?

Limiting Reactant

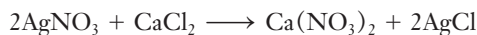
30.  Carbon monoxide and oxygen react to give carbon dioxide.



Imagine that we mix 8 CO molecules and 6 O_2 molecules and allow them to react as completely as possible.

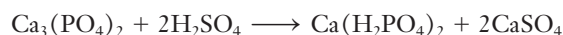
- Draw a molecular representation of the mixture of reactants.
- Draw a molecular representation of the product mixture, including any remaining reactant molecules.
- How many grams of CO_2 can be prepared from 134.67 g of CO and 77.25 g of O_2 ?

31.  Silver nitrate solution reacts with calcium chloride solution according to the equation



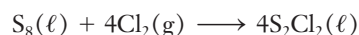
All of the substances involved in this reaction are soluble in water except silver chloride, AgCl , which forms a solid (precipitate) at the bottom of the flask. Suppose we mix together a solution containing 9.45 g of AgNO_3 and one containing 6.30 g of CaCl_2 . What mass of AgCl is formed?

32.  “Superphosphate,” a water-soluble fertilizer, is sometimes marketed as “triple phosphate.” It is a mixture of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and CaSO_4 on a 1:2 *mole* basis. It is formed by the reaction



We treat 200.0 g of $\text{Ca}_3(\text{PO}_4)_2$ with 133.5 g of H_2SO_4 . How many grams of superphosphate could be formed?

33. Gasoline is produced from crude oil, a nonrenewable resource. Ethanol is mixed with gasoline to produce a fuel called gasohol. Calculate the mass of water produced when 100.0 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is burned in 82.82 g of oxygen.
34. Disulfur dichloride, S_2Cl_2 , is used to vulcanize rubber. It can be made by treating molten sulfur with gaseous chlorine:



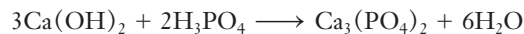
Starting with a mixture of 32.0 g of sulfur and 71.0 g of Cl_2 ,

- Which is the limiting reactant?
 - What is the theoretical yield of S_2Cl_2 ?
 - What mass of the excess reactant remains when the reaction is completed?
35. Silicon carbide, an abrasive, is made by the reaction of silicon dioxide with graphite.

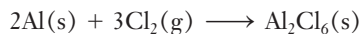


We mix 300. g of SiO_2 and 203 g of C. If the reaction proceeds as far as possible, which reactant is left over? How much of this reactant remains?

36. What is the maximum amount of $\text{Ca}_3(\text{PO}_4)_2$ that can be prepared from 12.9 g of $\text{Ca}(\text{OH})_2$ and 18.37 g of H_3PO_4 ?

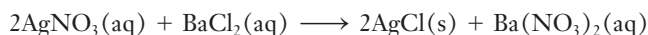


37. Aluminum chloride, Al_2Cl_6 , is an inexpensive reagent used in many industrial processes. It is made by treating scrap aluminum with chlorine according to the balanced equation



- Which reactant is limiting if 2.70 g Al and 4.05 g Cl_2 are mixed?
- What mass of Al_2Cl_6 can be produced?
- What mass of the excess reactant will remain when the reaction is complete?

38. The following equation represents a reaction between aqueous solutions of silver nitrate and barium chloride.



According to this equation, if a solution that contains 62.4 g AgNO_3 is mixed with a solution that contains 53.1 g BaCl_2 , (a) which is the limiting reactant? (b) How many grams of which reactant will be left over? (c) How many grams of AgCl will be formed?

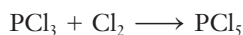
39. The following reaction takes place at high temperatures.



If 42.7 g Cr_2O_3 and 9.8 g Al are mixed and allowed to react until one of the reactants is used up, (a) which reactant will be left over? (b) How much will be left? (c) How many grams of chromium will be formed?

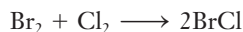
Percent Yield from Chemical Reactions

40. The percent yield for the reaction



is 76.5%. What mass of PCl_5 is obtained from the reaction of 92.5 g of PCl_3 with excess chlorine?

41. The percent yield for the following reaction carried out in carbon tetrachloride solution is 66.0%.



- (a) What amount of BrCl is formed from the reaction of 0.0350 mole of Br_2 with 0.0350 mole of Cl_2 ?

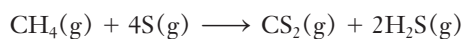
- (b) What amount of Br_2 is left unchanged?

42. When heated, potassium chlorate, KClO_3 , melts and decomposes to potassium chloride and diatomic oxygen.

- (a) What is the theoretical yield of O_2 from 5.79 g KClO_3 ?

- (b) If 1.05 g of O_2 is obtained, what is the percent yield?

43. The percent yield of the following reaction is consistently 92%.

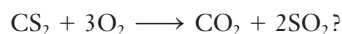


How many grams of sulfur would be needed to obtain 80.0 g of CS_2 ?

44. Solid silver nitrate undergoes thermal decomposition to form silver metal, nitrogen dioxide, and oxygen. Write the chemical equation for this reaction. A 0.665-g sample of silver metal is isolated from the decomposition of a 1.099-g sample of AgNO_3 . What is the percent yield of the reaction?

45. Tin(IV) chloride is produced in 81.1% yield by the reaction of tin with chlorine. How much tin is required to produce a kilogram of tin(IV) chloride?

46. What is the percent yield if 108 mg SO_2 is isolated from the combustion of 85.9 mg of carbon disulfide according to the reaction:

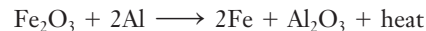


47. From a 45.0-g sample of an iron ore containing Fe_3O_4 , 1.56 g of Fe is obtained by the reaction:



What is the percent of Fe_3O_4 in the ore?

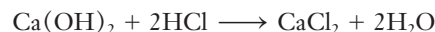
48. The reaction of finely divided aluminum and iron(III) oxide, Fe_2O_3 , is called the thermite reaction. It produces a tremendous amount of heat, making the welding of railroad track possible. The reaction of 500.0 grams of aluminum and 500.0 grams of iron(III) oxide produces 166.5 grams of iron. (a) Calculate the mass of iron that should be released by this reaction. (b) What is the percent yield of iron?



Charles D. Winters

Thermite reaction

49. Lime, $\text{Ca}(\text{OH})_2$, can be used to neutralize an acid spill. A 5.57-g sample of $\text{Ca}(\text{OH})_2$ reacts with an excess of hydrochloric acid; 7.41 g of calcium chloride is collected. What is the percent yield of this experiment?



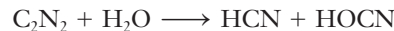
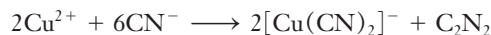
Sequential Reactions

50. Consider the two-step process for the formation of tellurous acid described by the following equations:



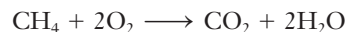
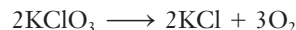
What mass of H_2TeO_3 is formed from 74.2 g of TeO_2 , assuming 100% yield?

51. Consider the formation of cyanogen, C_2N_2 , and its subsequent decomposition in water given by the equations

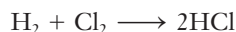
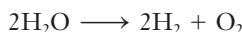


How much hydrocyanic acid, HCN , can be produced from 85.77 g of KCN , assuming 100% yield?

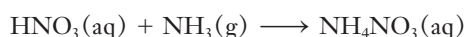
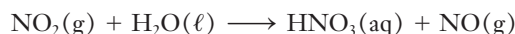
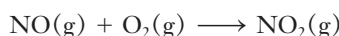
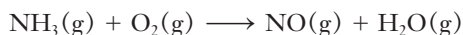
52. What mass of potassium chlorate is required to supply the proper amount of oxygen needed to burn 78.88 g of methane, CH_4 ?



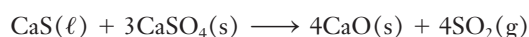
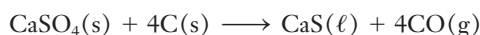
53. Hydrogen, obtained by the electrical decomposition of water, is combined with chlorine to produce 444.2 g of hydrogen chloride. Calculate the mass of water decomposed.



54. Ammonium nitrate, known for its use in agriculture, can be produced from ammonia by the following sequence of reactions:

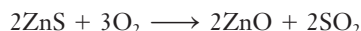


- (a) Balance each equation.
 (b) How many moles of nitrogen atoms are required for every mole of ammonium nitrate (NH_4NO_3)?
 (c) How much ammonia is needed to prepare 200.0 grams of ammonium nitrate (NH_4NO_3)?
55. Calcium sulfate is the essential component of plaster and sheet rock. Waste calcium sulfate can be converted into quicklime, CaO , by reaction with carbon at high temperatures. The following two reactions represent a sequence of reactions that might take place:



What weight of sulfur dioxide (in grams) could be obtained from 1.500 kg of calcium sulfate?

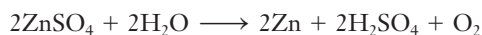
56. ▲ The chief ore of zinc is the sulfide, ZnS . The ore is concentrated by flotation and then heated in air, which converts the ZnS to ZnO .



The ZnO is then treated with dilute H_2SO_4



to produce an aqueous solution containing the zinc as ZnSO_4 . An electric current is passed through the solution to produce the metal.



What mass of Zn is obtained from an ore containing 454 kg of ZnS ? Assume the flotation process to be 89.6% efficient, the electrolysis step to be 92.2% efficient, and the other steps to be 100% efficient.

58. The density of an 18.0% solution of ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, is 1.10 g/mL. What mass of $(\text{NH}_4)_2\text{SO}_4$ is required to prepare 750.0 mL of this solution?
59. The density of an 18.0% solution of ammonium chloride, NH_4Cl , solution is 1.05 g/mL. What mass of NH_4Cl does 450. mL of this solution contain?
60. What volume of the solution of $(\text{NH}_4)_2\text{SO}_4$ described in Exercise 58 contains 125 g of $(\text{NH}_4)_2\text{SO}_4$?
61. ▲ A reaction requires 65.6 g of NH_4Cl . What volume of the solution described in Exercise 59 do you need if you want to use a 25.0% excess of NH_4Cl ?

Concentrations of Solutions—Molarity

62. What is the molarity of a solution prepared by dissolving 355 g of sodium phosphate, Na_3PO_4 , in water and diluting to 2.50 L of solution?
63. What is the molarity of a solution prepared by dissolving 4.49 g of sodium chloride in water and diluting to 40.0 mL of solution?
64. What volume of 0.123 M NaOH , in milliliters, contains 25.0 g NaOH ?
65. ● (a) Ethylene glycol, $\text{C}_2\text{H}_6\text{O}_2$ (antifreeze), is mixed with water in the radiators of cars to protect them against freezing. Draw a molecular representation of a solution of ethylene glycol in water. (Molecular models of ethylene glycol can be found in the margin of Section 2-1.)
 (b) How many kilograms of ethylene glycol, $\text{C}_2\text{H}_6\text{O}_2$, are needed to prepare a 9.00 M solution for use in a 12.0-L car radiator?



Charles D. Winters

Antifreeze being poured into water

66. A solution made by dissolving 16.0 g of CaCl_2 in 64.0 g of water has a density of 1.180 g/mL at 20°C. (a) What is the percent by mass of CaCl_2 in the solution? (b) What is the molarity of CaCl_2 in the solution?
67. A solution contains 0.100 mol/L of each of the following acids: HCl , H_2SO_4 , H_3PO_4 . (a) Is the molarity the same for each acid? (b) Is the number of molecules per liter the same for each acid? (c) Is the mass per liter the same for each acid? Give your reasoning in each case.
68. What is the molarity of a barium chloride solution prepared by dissolving 1.72 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in enough water to make 750. mL of solution?

Concentrations of Solutions—Percent by Mass

57. (a) How many moles of solute are contained in 500. g of a 15.00% aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$?
 (b) How many grams of solute are contained in the solution of part (a)?
 (c) How many grams of water (the solvent) are contained in the solution of part (a)?

69. How many grams of potassium benzoate trihydrate, $\text{KC}_7\text{H}_5\text{O}_2 \cdot 3\text{H}_2\text{O}$, are needed to prepare 1.0 L of a 0.150 *M* solution of potassium benzoate?
70. Stock hydrofluoric acid solution is 49.0% HF and has a specific gravity of 1.17. What is the molarity of the solution?
71. Stock phosphoric acid solution is 85.0% H_3PO_4 and has a specific gravity of 1.70. What is the molarity of the solution?

Dilution of Solutions

72. Commercial concentrated hydrochloric acid is 12.0 *M* HCl. What volume of concentrated hydrochloric acid is required to prepare 2.00 L of 1.50 *M* HCl solution?
73. Commercially available concentrated sulfuric acid is 18.0 *M* H_2SO_4 . Calculate the volume of concentrated sulfuric acid required to prepare 2.00 L of 1.50 *M* H_2SO_4 solution.
74. ▲ You want to clean a 1.00-L bottle that has been used to store a 0.500 *M* solution. Each time the bottle is emptied, 1.00 mL of solution adheres to the walls, and thus remains in the bottle. One method (method 1) of cleaning the bottle is to empty it, fill to 1.00 L with solvent, and then empty it again. An alternate method (method 2) is to empty the bottle, pour 9.00 mL of solvent into the bottle (to make 10.00 mL total), swirl to mix uniformly, and then empty it. This process is repeated twice, for a total of three rinses. (a) What is the concentration of the solution that remains in the flask after the single rinse in method 1? (b) What is the concentration of the solution that remains in the bottle after the triple rinse in method 2? (c) Compare these two methods of rinsing, in terms of the amount of solvent used. (d) Discuss the implications of this comparison for an industrial process in which many such bottles must be rinsed.
75. You want to clean a 0.500-L flask that has been used to store a 0.8 *M* solution. Each time the flask is emptied, 1.00 mL of solution adheres to the walls, and thus remains in the bottle. For each rinse cycle, you pour 9.00 mL of solvent into the flask (to make 10.00 mL total), swirl to mix uniformly, and then empty it. What is the minimum number of such rinses necessary to reduce the residual concentration to 0.0001 *M* (or below)?
76. Calculate the final volume of solution obtained if 100. mL of 12.0 *M* NaOH are diluted to 5.20 *M*.
77. In a laboratory preparation room one may find a reagent bottle containing 5.00 L of 12.0 *M* NaOH. Write a set of instructions for the production of 250. mL of 3.50 *M* NaOH from such a solution.
79. Calculate the number of grams of carbon dioxide, CO_2 , that can react with 54.55 mL of a 0.957 *M* solution of potassium hydroxide, KOH, according to the following reaction.
- $$2\text{KOH} + \text{CO}_2 \longrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$$
80. What volume of 0.558 *M* HNO_3 solution is required to react completely with 45.55 mL of 0.0515 *M* $\text{Ba}(\text{OH})_2$?
- $$\text{Ba}(\text{OH})_2 + 2\text{HNO}_3 \longrightarrow \text{Ba}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$$
81. What volume of 0.558 *M* HBr is required to react completely with 0.960 mole of $\text{Ca}(\text{OH})_2$?
- $$2\text{HBr} + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaBr}_2 + 2\text{H}_2\text{O}$$
82. An excess of AgNO_3 reacts with 110.5 mL of an AlCl_3 solution to give 0.215 g of AgCl. What is the concentration, in moles per liter, of the AlCl_3 solution?
- $$\text{AlCl}_3 + 3\text{AgNO}_3 \longrightarrow 3\text{AgCl} + \text{Al}(\text{NO}_3)_3$$
83. An impure sample of solid Na_2CO_3 is allowed to react with 0.1755 *M* HCl.
- $$\text{Na}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O}$$
- A 0.2337-g sample of sodium carbonate requires 15.55 mL of HCl solution. What is the purity of the sodium carbonate?

Mixed Exercises

84. ▲ An iron ore that contains Fe_3O_4 reacts according to the reaction



We obtain 2.11 g of Fe from the reaction of 75.0 g of the ore. What is the percent Fe_3O_4 in the ore?

85. ▲ If 86.3% of the iron can be recovered from an ore that is 43.2% magnetic iron oxide, Fe_3O_4 , what mass of iron could be recovered from 2.50 kg of this ore? The reduction of magnetic iron oxide is a complex process that can be represented in simplified form as

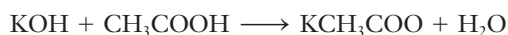


86. Gaseous chlorine will displace bromide ion from an aqueous solution of potassium bromide to form aqueous potassium chloride and aqueous bromine. Write the chemical equation for this reaction. What mass of bromine is produced if 0.631 g of chlorine undergoes reaction?
87. Calculate the volume of 2.25 *M* phosphoric acid solution necessary to react with 45.0 mL of 0.150 *M* $\text{Mg}(\text{OH})_2$.



Using Solutions in Chemical Reactions

78. Calculate the volume of a 0.157 *M* solution of potassium hydroxide, KOH, required to react with 0.385 g of acetic acid, CH_3COOH , according to the following reaction.

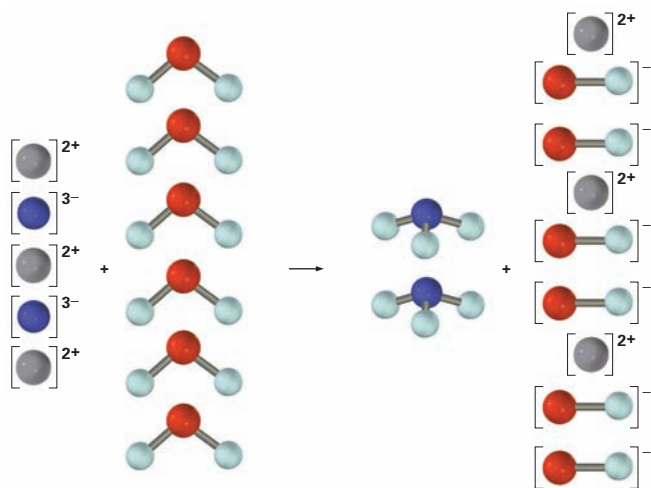


Conceptual Exercises

88. ● Using your own words, give a definition of a chemical reaction. Using drawings of ball-and-stick models, illustrate an example of a chemical reaction.

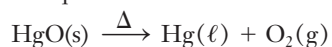


89. When magnesium metal is burned in air, most of it reacts with oxygen, producing magnesium oxide, MgO . However, at the high temperature of this reaction, some of the magnesium reacts with nitrogen in the air to produce magnesium nitride, Mg_3N_2 . This magnesium nitride can be eliminated by adding water, which reacts with the magnesium nitride to produce magnesium hydroxide, $\text{Mg}(\text{OH})_2$, and ammonia, NH_3 . The balanced equation for that reaction can be represented by the following:



For each element, verify that the same number of atoms appears on both sides of the equation. Write the balanced equation using molecular formulas.

90. A pink solution of cobalt(II) chloride is mixed with a colorless solution of potassium phosphate producing a suspended purple solid. Write the complete, balanced equation for this reaction. (Note: Most potassium salts are soluble and do not form suspensions.)
91. In 1774 Lavoisier repeated Priestley's experiment in which he discovered oxygen by heating red mercury(II) oxide. The unbalanced equation is:

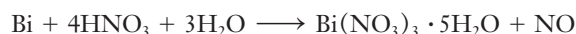


Balance this equation. Using the balanced equation, describe the amounts of each reactant and product in terms of atoms, molecules, and formula units (for any ionic compound). Then describe the amounts of each reactant and product in terms of moles. Finally, describe the amounts of each reactant and product in terms of mass, in grams. How did you determine the numbers of moles? Are the masses in the same proportions as the numbers of moles? Compare the mass of the mercury(II) oxide with the total mass of mercury and oxygen.

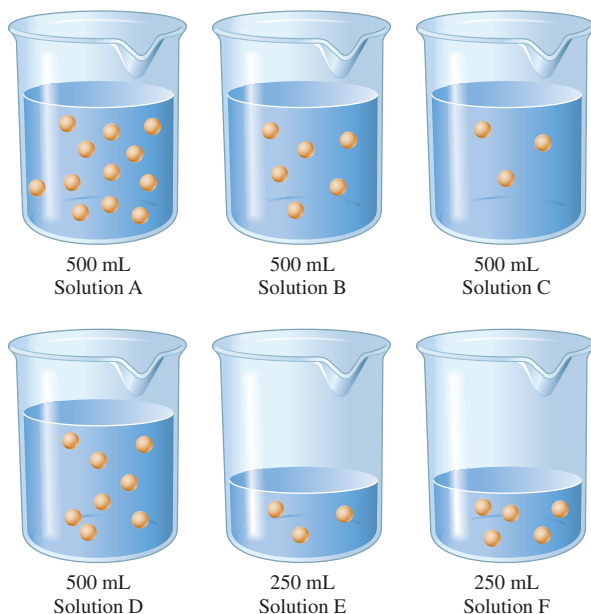
92. ● Beryllium nitride (Be_3N_2) is a gray solid that melts at 2200°C in the absence of air. (It reacts in air at 600°C .) It can be prepared by heating a mixture of beryllium powder and nitrogen gas at high temperatures. Write the complete, balanced equation for this reaction. How many moles of beryllium are required to react completely with

one mole of nitrogen? How many grams of beryllium are required to react completely with one gram of nitrogen? If the amount of beryllium is less than the amount of nitrogen, will the beryllium be the limiting reagent? In comparing those amounts, would you express them in moles or grams? Does it matter?

93. Write directions for the preparation of 1.000 L of 0.0500 M NaCl solution from a 0.558 M solution of NaCl.
94. Without making any calculations, arrange the following three solutions in order of increasing molarity. (a) 1.0% (by mass) NaCl; (b) 1.0% (by mass) SnCl_2 ; (c) 1.0% (by mass) AlCl_3 . (Assume that these solutions have nearly equal densities.)
95. To what volume must a student dilute 50. mL of a solution containing 25 mg of AlCl_3/mL so that the Al^{3+} concentration in the new solution is 0.022 M?
96. Bismuth dissolves in nitric acid according to the reaction below. What volume of 30.0% HNO_3 by mass (density = 1.182 g/mL) would be required to dissolve 20.0 g of Bi?



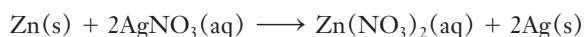
97. How would you prepare 1.00 L of 1.25×10^{-6} M NaCl (molecular weight 58.44 g/mol) solution by using a balance that can measure mass only to the nearest 0.01 g?
98. ● The drawings shown below represent beakers of aqueous solutions. Each sphere represents a dissolved solute particle.
- Which solution is most concentrated?
 - Which solution is least concentrated?
 - Which two solutions have the same concentration?
 - When solutions E and F are combined, the resulting solution has the same concentration as solution _____.



99. You prepared a NaCl solution by adding 58.44 g of NaCl to a 1-L volumetric flask and then adding water to dissolve it. When finished, the final volume in your flask looked like the illustration. The solution you prepared is
- greater than 1 M because you added more solvent than necessary.
 - less than 1 M because you added less solvent than necessary.
 - greater than 1 M because you added less solvent than necessary.
 - less than 1 M because you added more solvent than necessary.
 - 1 M because the amount of solute, not solvent, determines the concentration.

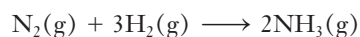


100. Zinc is more active chemically than is silver; it can be used to remove ionic silver from solution.

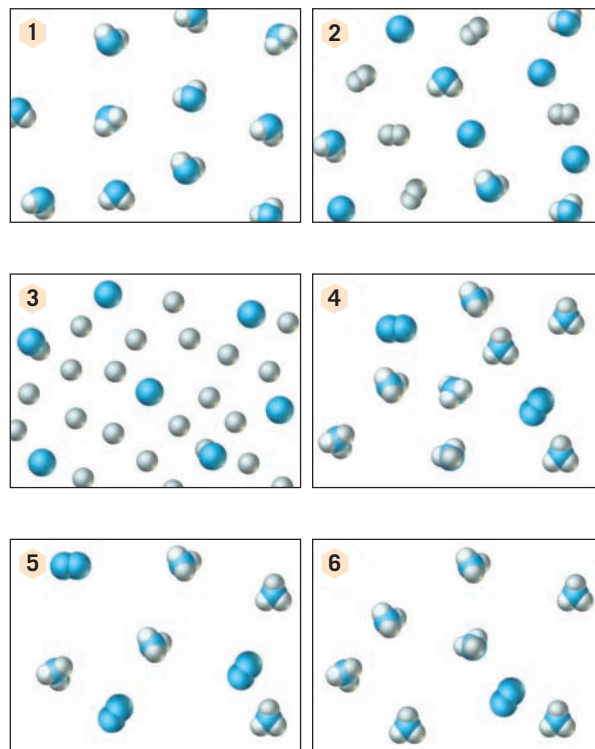
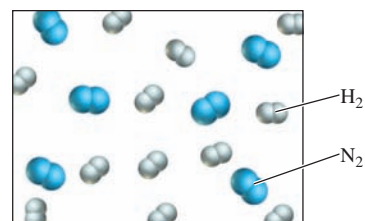


The concentration of a silver nitrate solution is determined to be 1.330 mol/L. Pieces of zinc totaling 100.0 g are added to 1.000 L of the solution; 90.0 g of silver is collected. (a) Calculate the percent yield of silver. (b) Suggest a reason why the yield is less than 100.0%.

101. Ammonia is formed in a direct reaction of nitrogen and hydrogen.

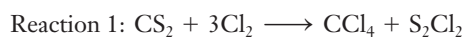


A tiny portion of the starting mixture is represented by the first diagram, where the blue spheres represent N and the white spheres represent H. Which of the numbered diagrams best represents the product mixture?

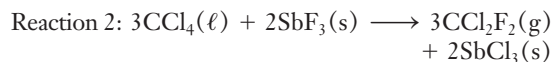


For the reaction of the given sample, which of the following is true?

- N_2 is the limiting reactant.
 - H_2 is the limiting reactant.
 - NH_3 is the limiting reactant.
 - No reactant is limiting; they are present in the correct stoichiometric ratio.
102. Given the amount of reactant used and the amount of product actually produced, how would you determine the theoretical amount of product and the percent yield? If the percent yield were calculated by using the number of moles of the product, would the result be the same as the percent yield calculated by using the mass of the product?
103. Carbon disulfide, CS_2 , reacts with chlorine, Cl_2 , in the presence of a catalyst at 105°C to 130°C , to form carbon tetrachloride, CCl_4 .



The carbon tetrachloride can react with antimony trifluoride, SbF_3 , to produce freon-12, CCl_2F_2 , a gas that was used in air conditioners.



If CCl_4 is produced from CS_2 (Reaction 1) with 62.5% yield and CCl_2F_2 is produced from CCl_4 (Reaction 2) with 71.5% yield, what mass of CS_2 must be chlorinated to obtain 125.0 grams of CCl_2F_2 from the CCl_4 produced?

Building Your Knowledge

104. Acetic acid, CH_3COOH , reacts with ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, to form ethyl acetate, $\text{CH}_3\text{COOCH}_2\text{CH}_3$, (density 0.902 g/mL) by the following reaction:



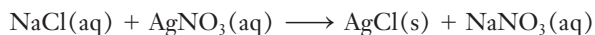
We combine 20.2 mL of acetic acid with 20.1 mL of ethanol.

- Which compound is the limiting reactant?
 - If 27.5 mL of pure ethyl acetate is produced, what is the percent yield? [Hint: See Tables 1-2 and 1-9.]
105. The following compounds are water-soluble. What ions are produced by each compound in aqueous solution?
- KOH
 - K_2SO_4
 - LiNO_3
 - $(\text{NH}_4)_2\text{SO}_4$
106. What is the molarity of a solution prepared by mixing 35.0 mL of 0.375 M NaCl solution with 47.5 mL of a 0.632 M NaCl solution?
107. ▲ Concentrated hydrochloric acid solution is 37.0% HCl and has a density of 1.19 g/mL. A dilute solution of HCl is prepared by diluting 4.50 mL of this concentrated HCl solution to 100.00 mL with water. Then 10.0 mL of this dilute HCl solution reacts with an AgNO_3 solution according to the following reaction:



How many milliliters of 0.1105 M AgNO_3 solution is required to precipitate all of the chloride as $\text{AgCl}(\text{s})$?

108. In a particular experiment, 225 g of phosphorus, P_4 , reacted with excess oxygen to form tetraphosphorus decoxide, P_4O_{10} , in 89.5% yield. In a second step reaction with water, a 97.8% yield of H_3PO_4 was obtained.
- Write the balanced equations for these two reaction steps.
 - What mass of H_3PO_4 was obtained?
109. ▲ A mixture of potassium chloride and potassium bromide weighing 3.595 g is heated with chlorine, which converts the KBr completely to potassium chloride. The total mass of potassium chloride after the reaction is 3.129 g. What percentage of the original mixture was potassium bromide?
110. What mass of AgCl could be formed by mixing 10.0 mL of a 1.20% NaCl by mass solution ($D = 1.02 \text{ g/mL}$) with 50.0 mL of $1.21 \times 10^{-2} \text{ M AgNO}_3$? The chemical equation for the reaction of these two solutions is:

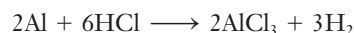
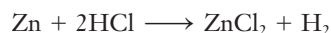


111. Magnesium displaces copper from a dilute solution of copper(II) sulfate; the pure copper will settle out of the solution.



A copper(II) sulfate solution is mixed by dissolving 25.000 g of copper(II) sulfate, and then it is treated with an excess of magnesium metal. The mass of copper collected is 8.786 g after drying. Calculate the percent yield of copper.

112. Suppose you are designing an experiment for the preparation of hydrogen. For the production of equal amounts of hydrogen, which metal, Zn or Al, is less expensive if Zn costs about half as much as Al on a mass basis?



113. Gaseous chlorine and gaseous fluorine undergo a combination reaction to form the interhalogen compound ClF .
- Write the chemical equation for this reaction.
 - Calculate the mass of fluorine needed to react with 3.47 g of Cl_2 .
 - How many grams of ClF are formed?

Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

114. Use an internet search engine (such as <http://www.google.com>) to locate “drinking water standards” or locate the standards at www.epa.gov/safewater. List four inorganic contaminants in drinking water and their maximum contaminant levels (MCLs) allowed.
115. Using the website found in Exercise 114 or another website, list the potential health effects from ingestion of drinking water with excess (a) copper; (b) cadmium.
116. Using the website found in Exercise 114 or another website, list the potential health effects from ingestion of drinking water with excess (a) antimony; (b) beryllium.
117. Consider the websites used in Exercise 114. What is the molarity of the copper atoms or ions in a drinking water sample that has a concentration of copper just equal to the indicated MCLs (maximum contamination levels) allowed for copper in drinking water?
118. There has been considerable controversy over the addition of fluoride (typically in the form of NaF) to drinking water. Fluoridation strengthens tooth enamel, making it more resistant to decay. Search the web to find typical concentrations of fluoride in water that are used for fluoridation. Convert the ppm (or ppb) concentration you find to molarity.

The Structure of Atoms

4



The Lagoon nebula taken by NASA's Spitzer Space Telescope. Atomic excited state emissions produce the following colors in *visible* spectrum photos: red (hydrogen, oxygen), green (oxygen), blue (doubly ionized oxygen, nitrogen), violet (nitrogen). This photo, however, was taken in the infrared region so the colors are “false” (computer assigned) and correspond to different infrared frequencies. Here most of the infrared radiation is coming from carbon atoms that are heated by the stars in the central area.

NASA/JPL-Caltech

OUTLINE

Subatomic Particles

- 4-1 Fundamental Particles
- 4-2 The Discovery of Electrons
- 4-3 Canal Rays and Protons
- 4-4 Rutherford and the Nuclear Atom
- 4-5 Atomic Number
- 4-6 Neutrons
- 4-7 Mass Number and Isotopes
- 4-8 Mass Spectrometry and Isotopic Abundance
- 4-9 The Atomic Weight Scale and Atomic Weights
- 4-10 The Periodic Table: Metals, Nonmetals, and Metalloids

The Electronic Structures of Atoms

- 4-11 Electromagnetic Radiation
- 4-12 The Photoelectric Effect
- 4-13 Atomic Spectra and the Bohr Atom
- 4-14 The Wave Nature of the Electron
- 4-15 The Quantum Mechanical Picture of the Atom
- 4-16 Quantum Numbers
- 4-17 Atomic Orbitals
- 4-18 Electron Configurations
- 4-19 The Periodic Table and Electron Configurations
- 4-20 Paramagnetism and Diamagnetism

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Describe the evidence for the existence and properties of electrons, protons, and neutrons
- ▶ Predict the arrangements of the particles in atoms
- ▶ Describe isotopes and their composition
- ▶ Calculate atomic weights from isotopic abundance
- ▶ Describe the periodic table and some of the relationships that it summarizes
- ▶ Describe the wave properties of light and how wavelength, frequency, and speed are related
- ▶ Use the particle description of light, and explain how it is related to the wave description
- ▶ Relate atomic emission and absorption spectra to important advances in atomic theory
- ▶ Describe the main features of the quantum mechanical picture of the atom
- ▶ Describe the four quantum numbers, and give possible combinations of their values for specific atomic orbitals
- ▶ Describe the shapes of orbitals and recall the usual order of their relative energies
- ▶ Write the electron configurations of atoms
- ▶ Relate the electron configuration of an atom to its position in the periodic table

The Dalton theory of the atom and related ideas were the basis for our study of *composition stoichiometry* (see Chapter 2) and *reaction stoichiometry* (see Chapter 3). That level of atomic theory, however, leaves many questions unanswered. *Why* do atoms combine to form compounds? *Why* do they combine only in simple numerical ratios? *Why* are particular numerical ratios of atoms observed in compounds? *Why* do different elements have different properties? *Why* are they gases, liquids, solids, metals, nonmetals, and so on? *Why* do some groups of elements have similar properties and form compounds with similar formulas? The answers to these and many other important questions in chemistry are supplied by our modern understanding of the nature of atoms. But how can we study something as small as an atom?

Much of the development of modern atomic theory was based on two broad types of research carried out by dozens of scientists just before and after 1900. The first type dealt with the electrical nature of matter. These studies led scientists to recognize that atoms are composed of more fundamental particles and helped them to describe the approximate arrangements of these particles in atoms. The second broad area of research dealt with the interaction of matter with energy in the form of light. Such research included studies of the colors of the light that substances give off or absorb. These studies led to a much more detailed understanding of the arrangements of particles in atoms. It then became clear that the arrangement of the particles determines the chemical and physical properties of each element. As we learn more about the structures of atoms, we are able to organize chemical facts in ways that help us to understand the behavior of matter.

We will first study the particles that make up atoms, and the basic structure of atoms, along with some history and the organization of the periodic table of elements. Then we will take a look at the quantum mechanical theory of atoms and see how this theory describes the arrangement of the electrons in atoms. Current atomic theory is by no means complete. Even so, it is a powerful tool that helps us describe the bonding forces that hold atoms together to form the vast array of matter that makes up the universe.

▶ Accounts of some important developments in atomic theory appear on the World Wide Web; for example, an interesting online history of the discovery of the electron is at www.aip.org/history/electron

Subatomic Particles

4-1 Fundamental Particles

▶ Many other subatomic particles, such as quarks, positrons, neutrinos, pions, and muons, have also been discovered. It is not necessary to study their characteristics to understand the fundamentals of atomic structure that are important for chemical properties.

In our study of atomic structure, we look first at the **fundamental particles**. Atoms, and hence *all* matter, consist principally of three fundamental particles: *electrons*, *protons*, and *neutrons*, which are the basic building blocks for atomic structure. Knowledge of the nature and functions of these particles is essential for understanding chemical interactions.

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 4-1 Fundamental Particles of Matter

Particle	Mass	Charge (relative scale)
electron (e^-)	0.00054858 amu	1−
proton (p or p^+)	1.0073 amu	1+
neutron (n or n^0)	1.0087 amu	none

The relative masses and charges of the three fundamental particles are shown in Table 4-1. The mass of an electron is very small compared with the mass of either a proton or a neutron. The charge on a proton is equal in magnitude, but opposite in sign, to the charge on an electron. Let's examine these particles in more detail.

4-2 The Discovery of Electrons

Some of the earliest evidence about atomic structure was supplied in the early 1800s by the English chemist Humphry Davy (1778–1829). He found that when he passed electric current through some substances, the substances decomposed. He therefore suggested that the elements of a chemical compound are held together by electrical forces. In 1832–1833, Michael Faraday (1791–1867), who was Davy's student, determined the quantitative relationship between the amount of electricity used in electrolysis and the amount of chemical reaction that occurs. Studies of Faraday's work by George Stoney (1826–1911) led him to suggest in 1874 that units of electric charge are associated with atoms. In 1891, he suggested that these electrical charges be named *electrons*.

The most convincing evidence for the existence of electrons came from experiments using **cathode-ray tubes** (Figure 4-1). Two electrodes are sealed in a glass tube containing gas at a very low pressure. When a high voltage is applied, current flows and rays are given off by the cathode (negative electrode). These rays travel in straight lines toward the anode (positive electrode) and cause the walls opposite the cathode to glow. An object placed in the path of the cathode rays casts a shadow on a zinc sulfide fluorescent screen placed near the anode. The shadow shows that the rays travel from the negatively charged cathode toward the positively charged anode. This tells us that the rays must be negatively charged. Furthermore, they are deflected by electric and magnetic fields in the directions expected for negatively charged particles.

In 1897 J. J. Thomson (1856–1940) studied these negatively charged particles more carefully. He called them **electrons**, as Stoney had suggested. By studying the degree of deflections of cathode rays in different strengths of electric and magnetic fields, Thomson determined the ratio of the charge (e) of the electron to its mass (m). The modern value for this ratio (to six significant figures) is

$$e/m = 1.75882 \times 10^8 \text{ coulomb (C)/g}$$

This ratio is the same regardless of the type of gas in the tube, the composition of the electrodes, or the nature of the electric power source. Thomson's work suggested that electrons are fundamental particles that are present in all atoms. We now know that this is true and that all atoms contain integral (whole) numbers of electrons.

After the charge-to-mass ratio for the electron had been determined, additional experiments were necessary to determine the value of either its mass or its charge so that the other could be calculated. In 1909, Robert Millikan (1868–1953) solved this dilemma with the famous "oil-drop experiment," in which he determined the charge of the electron. This experiment is described in Figure 4-2. All of the charges measured by Millikan turned out to be integral multiples of the same number. He assumed that this smallest charge was the charge on one electron. This value is 1.60218×10^{-19} coulomb (modern value to six significant figures).

► The process is called chemical electrolysis. *Lysis* means "splitting apart."

► Study Figures 4-1 and 4-2 as you read this section.

► The coulomb (C) is the standard unit of *quantity* of electric charge. It is defined as the quantity of electricity transported in one second by a current of one ampere. It corresponds to the amount of electricity that will deposit 0.00111798 g of silver in an apparatus set up for plating silver.

► The charge on one mole (Avogadro's number) of electrons is 96,485 coulombs.

Unless otherwise noted, all content on this page is © Cengage Learning.

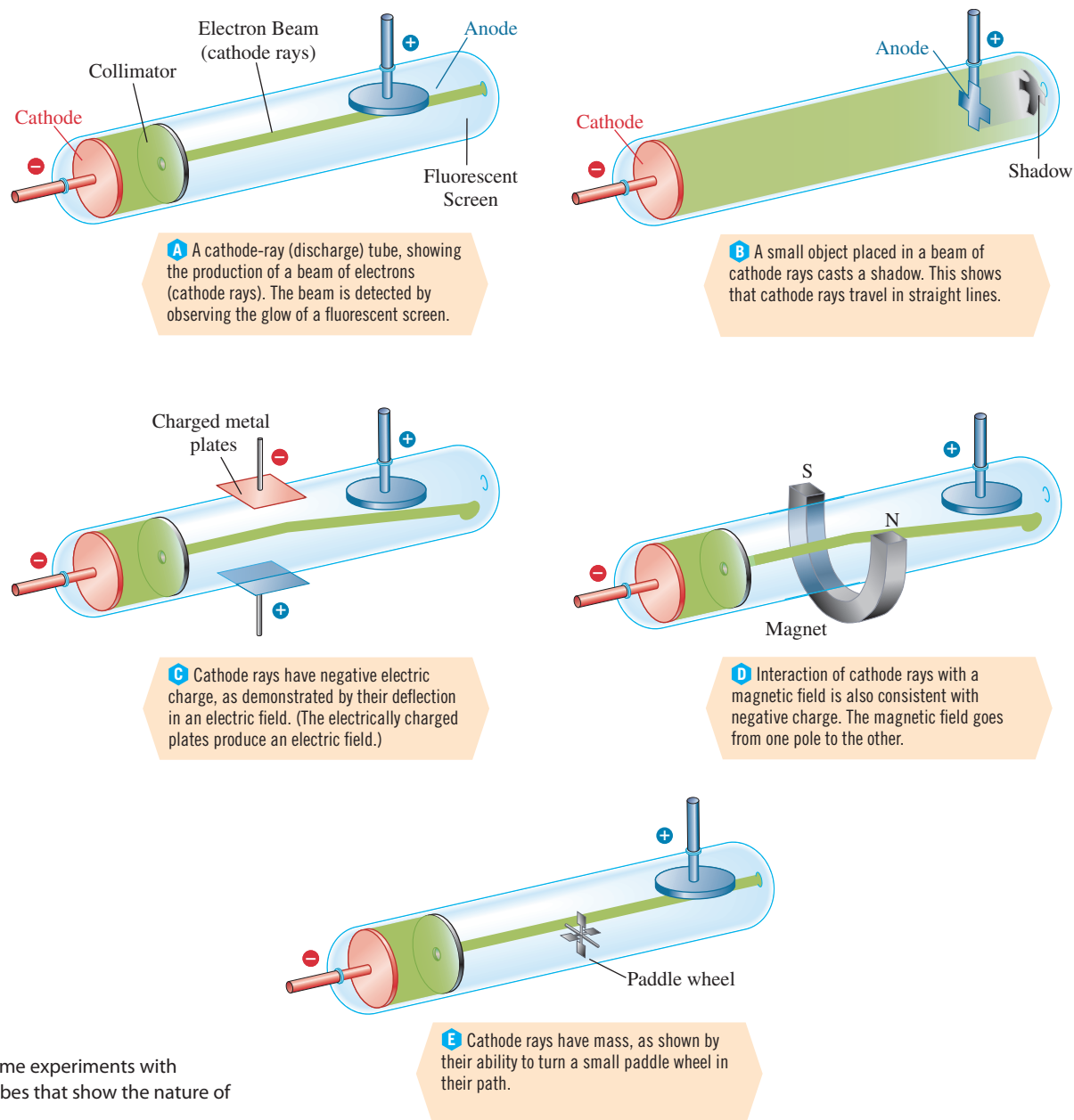


Figure 4-1 Some experiments with cathode-ray tubes that show the nature of cathode rays.

The charge-to-mass ratio, $e/m = 1.75882 \times 10^8 \text{ C/g}$, can be used in inverse form to calculate the mass of the electron:

$$m = \frac{1 \text{ g}}{1.75882 \times 10^8 \text{ C}} \times 1.60218 \times 10^{-19} \text{ C}$$

$$= 9.10940 \times 10^{-28} \text{ g}$$

► The value of e/m obtained by Thomson and the values of e and m obtained by Millikan differ slightly from the modern values given in this text because early measurements were not as accurate as modern ones.

This is only about 1/1836 the mass of a hydrogen atom, the lightest of all atoms. Millikan's simple oil-drop experiment stands as one of the cleverest, yet most fundamental, of all classic scientific experiments. It was the first experiment to suggest that atoms contain integral numbers of electrons; we now know this to be true.

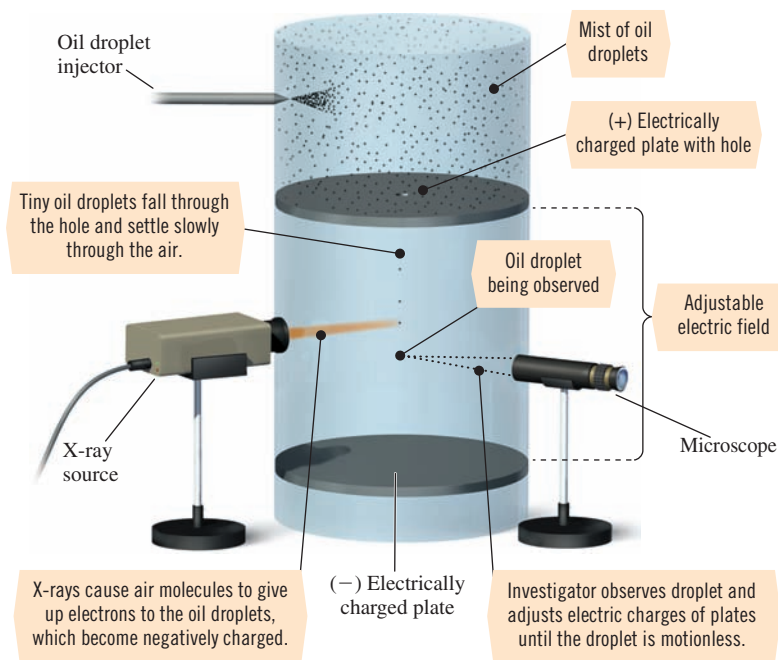
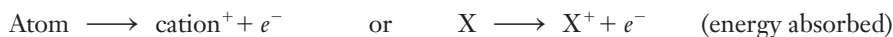


Figure 4-2 The Millikan oil-drop experiment. Tiny spherical oil droplets are produced by an atomizer. The mass of the spherical drop can be calculated from its volume (obtained from a measurement of the radius of the drop with a microscope) and the known density of the oil. A few droplets fall through the hole in the upper plate. Irradiation with X-rays gives some of these oil droplets a negative charge. When the voltage between the plates is increased, a negatively charged drop falls more slowly because it is attracted by the positively charged upper plate and repelled by the negatively charged lower plate. At one particular voltage, the electrical force (up) and the gravitational force (down) on the drop are exactly balanced, and the drop remains stationary. Knowing this voltage and the mass of the drop, we can calculate the charge on the drop.

4-3 Canal Rays and Protons

In 1886 Eugen Goldstein (1850–1930) first observed that a cathode-ray tube also generates a stream of positively charged particles that moves toward the cathode. These were called **canal rays** because they were observed occasionally to pass through a channel, or “canal,” drilled in the negative electrode (Figure 4-3). These *positive rays*, or *positive ions*, are created when the gaseous atoms in the tube lose electrons. Positive ions are formed by the process



Different elements give positive ions with different e/m ratios. The regularity of the e/m values for different ions led to the idea that there is a subatomic particle with one unit of positive charge, called the **proton**. The proton is a fundamental particle with a charge equal in magnitude but opposite in sign to the charge on the electron. Its mass is almost 1836 times that of the electron.

► The proton was observed by Ernest Rutherford and James Chadwick in 1919 as a particle that is emitted by bombardment of certain atoms with α -particles.

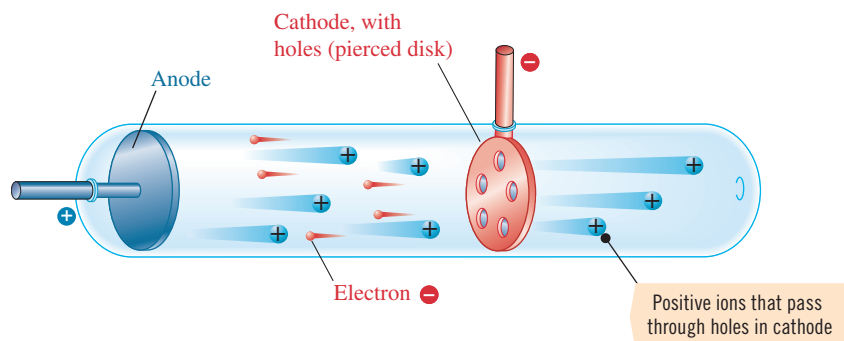


Figure 4-3 A cathode-ray tube with a different design and with a perforated cathode. Such a tube was used to produce canal rays and to demonstrate that they travel toward the cathode. Like cathode rays, these *positive rays* are deflected by electric or magnetic fields, but in the opposite direction from cathode rays (electron beam). Canal ray particles have e/m ratios many times smaller than those of electrons because of their much greater masses. When different elements are in the tube, positive ions with different e/m ratios are observed.

4-4 Rutherford and the Nuclear Atom

By the early 1900s, it was clear that each atom contains regions of both positive and negative charge. The question was, how are these charges arranged? The dominant view of that time was summarized in J. J. Thomson's model of the atom; the positive charge was thought to be distributed evenly throughout the atom. The negative charges were pictured as being imbedded in the atom like plums in a pudding (the "plum pudding model").

Soon after Thomson developed his model, great insight into atomic structure was provided by one of his former students, Ernest Rutherford (1871–1937), the outstanding experimental physicist of his time.

By 1909, Rutherford had established that alpha- (α -) particles are positively charged particles. They are emitted at high kinetic energies by some radioactive atoms, that is, atoms that disintegrate spontaneously. In 1910 Rutherford's research group carried out a series of experiments that had an enormous impact on the scientific world. They bombarded a very thin piece of gold foil with α -particles from a radioactive source. A fluorescent zinc sulfide screen was placed around the foil to indicate the scattering of the α -particles by the gold foil (Figure 4-4). Scintillations (flashes) on the screen, caused by the individual α -particles, were counted to determine the relative numbers of α -particles deflected at various angles. At the time, α -particles were believed to be extremely dense, much denser than the gold atom.

If the Thomson model of the atom were correct, any α -particles passing through the foil would have been deflected by very small angles. Quite unexpectedly, nearly all of the α -particles passed through the foil with little or no deflection. A few, however, were deflected through large angles, and a very small number of α -particles even returned from the gold foil in the direction from which they had come! Rutherford was astounded. In his own words,

It was quite the most incredible event that has ever happened to me in my life. It was almost as if you fired a 15-inch shell into a piece of tissue paper and it came back and hit you.

Rutherford's mathematical analysis of his results showed that the scattering of positively charged α -particles was caused by repulsion from very dense regions of positive charge in the gold foil. He concluded that the mass of one of these regions is nearly equal to that of a gold atom, but that the diameter is no more than 1/10,000 that of an



© The Print Collector/Alamy

Ernest Rutherford was one of the giants in the development of our understanding of atomic structure. While working with J. J. Thomson at Cambridge University, he discovered α - and β -radiation. He spent the years 1899–1907 at McGill University in Canada where he proved the nature of these two radiations, for which he received the Nobel Prize in chemistry in 1908. He returned to England in 1908, and it was there, at Manchester University, that he and his coworkers Hans Geiger and Ernst Marsden performed the famous gold foil experiments that led to the nuclear model of the atom. Not only did he perform much important research in physics and chemistry, but he also guided the work of ten future recipients of the Nobel Prize.

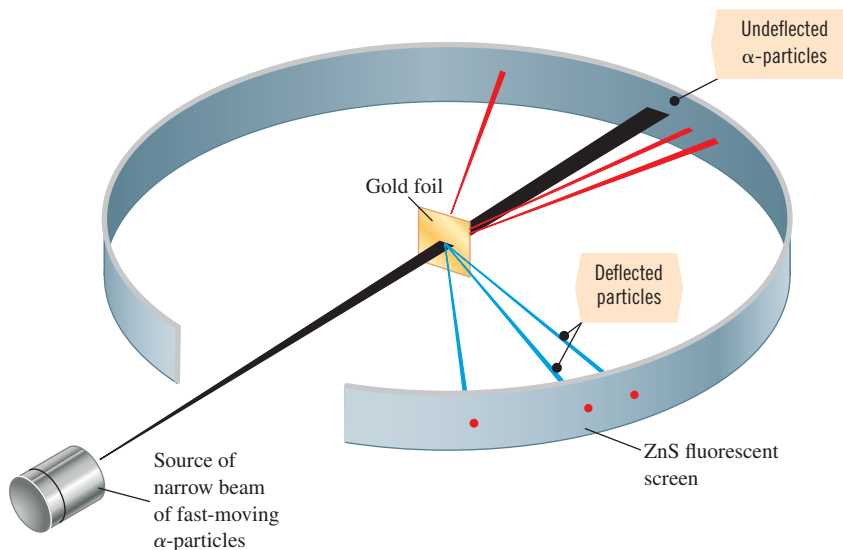
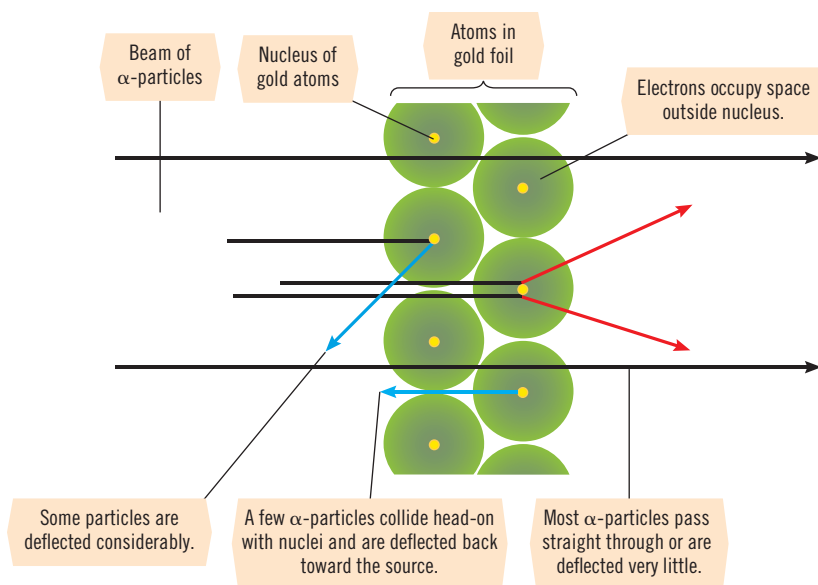


Figure 4-4 The Rutherford scattering experiment. A narrow beam of α -particles from a radioactive source was directed at a very thin sheet of gold foil. Most of the particles passed through the gold foil with no deflection (shown in black). Many were deflected through moderate angles (shown in red). These deflections were surprising, but the 0.001% of the total that were reflected at acute angles (shown in blue) were totally unexpected.



► This representation is *not* to scale. If nuclei were as large as the dots that represent them, each region that represents the size of an atom would have a diameter of more than 100 feet!

Figure 4-5 An interpretation of the Rutherford scattering experiment. The atom is pictured as consisting mostly of “open” space. The electrons are thinly distributed throughout the “open” space. Most of the positively charged α -particles (black arrows) pass through the open space undeflected, not coming near any gold nuclei. The few that pass fairly close to a nucleus (red arrows) are repelled by electrostatic forces and thereby deflected. The very few particles that are on a path to collide with gold nuclei are repelled backward at acute angles (blue arrows).

atom. Many experiments with foils of different metals yielded similar results. Realizing that these observations were inconsistent with previous theories about atomic structure, Rutherford discarded the old theory and proposed a better one. He suggested that each atom contains a *tiny, but massive, positively charged center* that he called the atomic **nucleus**. Most α -particles pass through metal foils undeflected because atoms are *primarily* empty space populated only by the very light electrons. The few particles that are deflected are the ones that come close to the heavy, highly charged metal nuclei (Figure 4-5).

Rutherford was able to determine the magnitudes of the positive charges on the atomic nuclei. The picture of atomic structure that he developed is called the Rutherford model of the atom.

Atoms consist of very small, very dense positively charged nuclei surrounded by clouds of electrons at relatively large distances from the nuclei.

4-5 Atomic Number

Only a few years after Rutherford's scattering experiments, H. G. J. Moseley (1887–1915) studied X-rays given off by various elements. Max von Laue (1879–1960) had shown that X-rays could be diffracted by crystals into a spectrum in much the same way that visible light can be separated into its component colors. X-rays can be generated by aiming a beam of high-energy electrons at a solid target made of a single pure element (Figure 4-6a).

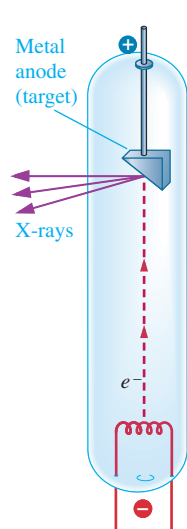
The spectra of X-rays produced by targets of different elements were recorded photographically. Each photograph consisted of a series of lines representing X-rays at various wavelengths; each element produced its own distinct set of wavelengths. Comparison of results from different elements revealed that corresponding lines were displaced toward shorter wavelengths as atomic weights of the target materials increased, with a few exceptions. But in 1913 Moseley showed that the X-ray wavelengths could be better correlated

► In a modern technique known as “X-ray fluorescence spectroscopy,” the wavelengths of X-rays given off by a sample target indicate which elements are present in the sample.

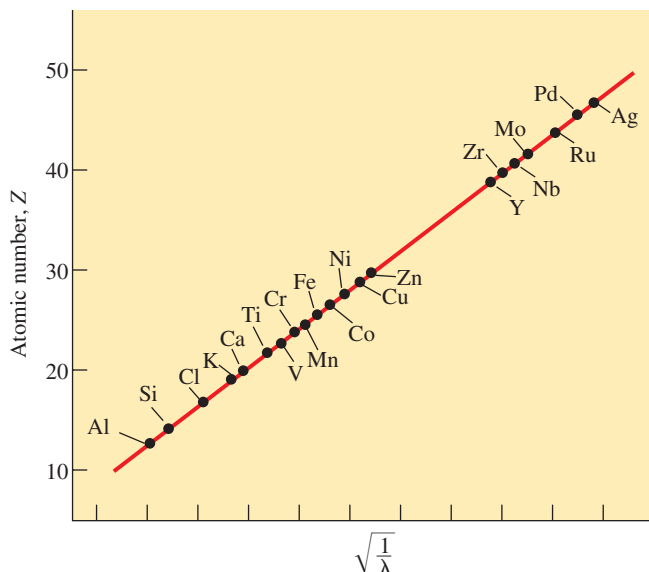
Unless otherwise noted, all content on this page is © Cengage Learning.



H. G. J. Moseley was one of the many remarkable scientists who worked with Ernest Rutherford. Moseley's scientific career was very short. He enlisted in the British army during World War I and died in battle in the Gallipoli campaign in 1915.



A A simplified representation of the production of X-rays by bombardment of a solid target with a high-energy beam of electrons.



B A plot of some of Moseley's X-ray data. The atomic number of an element is found to be directly proportional to the square root of the reciprocal of the wavelength of a particular X-ray spectral line. Wavelength (see Section 4-10) is represented by λ .

Figure 4-6 Production of X-rays and effect of atomic number on wavelength.

with the atomic number. A plot illustrating this interpretation of Moseley's data appears in Figure 4-6b. On the basis of his mathematical analysis of these X-ray data, he concluded that

each element differs from the preceding element by having one more positive charge in its nucleus.

For the first time it was possible to arrange all known elements in order of increasing nuclear charge. This discovery led to the realization that atomic number, related to the electrical properties of the atom, was more fundamental to determining the properties of the elements than atomic weight was. This discovery put the ideas of the periodic table on a more fundamental footing.

We now know that every nucleus contains an integral number of protons exactly equal to the number of electrons in a neutral atom of the element. Every hydrogen nucleus contains one proton, every helium nucleus contains two protons, every lithium nucleus contains three protons, and so on.

The number of protons in the nucleus of an atom determines its identity; this number is known as the **atomic number** of that element.

► This does not mean that elements above number 19 do not have neutrons, only that neutrons are not generally knocked out of atoms of higher atomic number by α -particle bombardment until one reaches the radioactive actinide elements and beyond.

4-6 Neutrons

The third fundamental particle, the neutron, eluded discovery until 1932. James Chadwick (1891–1974) correctly interpreted experiments on the bombardment of beryllium with high-energy α -particles. Later experiments showed that nearly all ele-

ments up to potassium, element 19, produce neutrons when they are bombarded with high-energy α -particles. The **neutron** is an uncharged particle with a mass slightly greater than that of the proton.

Atoms consist of very small, very dense nuclei surrounded by clouds of electrons at relatively great distances from the nuclei. All nuclei contain protons; nuclei of all atoms except the common form of hydrogen also contain neutrons.

Nuclear diameters are about 10^{-5} nanometers (nm); atomic diameters are about 10^{-1} nm. To put this difference in perspective, suppose that you wish to build a model of an atom using a basketball (diameter about 9.5 inches) as the nucleus; on this scale, the atomic model would be nearly 6 miles across!

4-7 Mass Number and Isotopes

Most elements consist of atoms of different masses, called **isotopes**. The isotopes of a given element contain the same number of protons (and also the same number of electrons) because they are atoms of the same element. They differ in mass because they contain different numbers of neutrons in their nuclei.

Isotopes are atoms of the same element with different masses; they are atoms containing the same number of protons but different numbers of neutrons.

For example, there are three distinct kinds of hydrogen atoms, commonly called hydrogen, deuterium, and tritium. (This is the only element for which we give each isotope a different name.) Each contains one proton in the atomic nucleus. The predominant form of hydrogen contains no neutrons, but each deuterium atom contains one neutron and each tritium atom contains two neutrons in its nucleus (Table 4-2). All three forms of hydrogen display very similar chemical properties.

The **mass number** of an atom is the sum of the number of protons and the number of neutrons in its nucleus; that is

$$\begin{aligned}\text{Mass number} &= \text{number of protons} + \text{number of neutrons} \\ &= \text{atomic number} + \text{neutron number}\end{aligned}$$

► A mass number is a count of the *number* of protons plus neutrons present, so it must be a whole number. Because the masses of the proton and the neutron are both about 1 amu, the mass number is *approximately* equal to the actual mass of the isotope (which is not a whole number).

The mass number for normal hydrogen atoms is 1; for deuterium, 2; and for tritium, 3. The composition of a nucleus is indicated by its **nuclide symbol**. This consists of the symbol for the element (*E*), with the atomic number (*Z*) written as a subscript at the lower left and the mass number (*A*) as a superscript at the upper left, ${}^A_Z E$ (Figure 4-7). By this system, the three isotopes of hydrogen are designated as ${}^1_1\text{H}$, ${}^2_1\text{H}$, and ${}^3_1\text{H}$.

Table 4-2 The Three Isotopes of Hydrogen

Name	Symbol	Nuclide Symbol	Mass (amu)	Atomic Abundance in Nature	No. of Protons	No. of Neutrons	No. of Electrons (in neutral atoms)
hydrogen	H	${}^1_1\text{H}$	1.007825	99.985%	1	0	1
deuterium	D	${}^2_1\text{H}$	2.01400	0.015%	1	1	1
tritium*	T	${}^3_1\text{H}$	3.01605	0.000%	1	2	1

*No known natural sources; produced by decomposition of artificial isotopes.

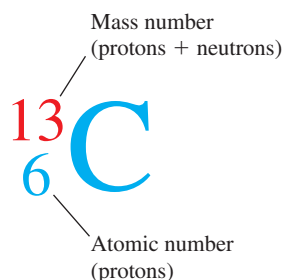


Figure 4-7 Interpretation of a nuclide symbol. Chemists often omit the subscripted atomic number because the element symbol implies the atomic number.

STOP & THINK

Isotopes of an element differ only in the number of neutrons they contain.

EXAMPLE 4-1 Determination of Atomic Makeup

Determine the number of protons, neutrons, and electrons in each of the following species. Are the members within each pair isotopes?

- (a) $^{35}_{17}\text{Cl}$ and $^{37}_{17}\text{Cl}$ (b) $^{63}_{29}\text{Cu}$ and $^{65}_{29}\text{Cu}$

Plan

We know that the number at the bottom left of the nuclide symbol is the atomic number or number of protons. This lets us verify the identity of the element in addition to knowing the number of protons per nuclide. From the mass number at the top left, we know the number of protons plus neutrons. The number of protons (atomic number) minus the number of electrons must equal the charge, if any, shown at the top right. From these data one can determine if two nuclides have the same number of protons and are therefore the same element. If they are the same element, they will be isotopes only if their mass numbers differ.

Solution

- (a) For $^{35}_{17}\text{Cl}$: Atomic number = 17. There are therefore 17 protons per nucleus. Mass number = 35. There are therefore 35 protons plus neutrons or, because we know that there are 17 protons, there are 18 neutrons. Because no charge is indicated, there must be equal numbers of protons and electrons, or 17 electrons.

For $^{37}_{17}\text{Cl}$: There are 17 protons, 20 neutrons, and 17 electrons per atom.

These are isotopes of the same element. Both have 17 protons, but they differ in their numbers of neutrons: one has 18 neutrons and the other has 20.

- (b) For $^{63}_{29}\text{Cu}$: Atomic number = 29. There are 29 protons per nucleus. Mass number = 63. There are 29 protons plus 34 neutrons. Because no charge is indicated, there must be equal numbers of protons and electrons, or 29 electrons.

For $^{65}_{29}\text{Cu}$: There are 29 protons, 36 neutrons, and 29 electrons per atom.

These are isotopes. Both have 29 protons, but they differ in their numbers of neutrons: one isotope has 34 neutrons and the other has 36.

You should now work Exercises 18 and 20.

4-8 Mass Spectrometry and Isotopic Abundance

Mass spectrometers are instruments that measure the charge-to-mass ratio of charged particles. A gas sample at very low pressure is bombarded with high-energy electrons. This causes electrons to be ejected from some of the gas molecules, creating positive ions. The positive ions are then focused into a very narrow beam and accelerated by an electric field. One type of mass spectrometer uses a magnetic field to deflect the ions from their straight-line path (Figure 4-8). The extent to which the beam of ions is deflected depends on four factors:

1. *Magnitude of the accelerating voltage (electric field strength).* Higher voltages result in beams of more rapidly moving particles that are deflected less than the beams of the more slowly moving particles produced by lower voltages.
2. *Magnetic field strength.* Stronger fields deflect a given beam more than weaker fields.
3. *Masses of the particles.* Because of their inertia, heavier particles are deflected less than lighter particles that carry the same charge.
4. *Charges on the particles.* Particles with higher charges interact more strongly with magnetic fields and are thus deflected more than particles of equal mass with smaller charges.

► Newer mass spectrometers use a simple time-of-flight detector that measures the time the positively charged particles take to travel to the part of the detector that records the impact of the ion. The longer a particle takes to travel the distance, the greater its mass. Another common type of mass spectrometer uses a quadrupole electrostatic field to sort ions by their masses.

The mass spectrometer can be used to measure masses of isotopes as well as isotopic abundances, that is, the relative amounts of the isotopes. Helium occurs in nature almost exclusively as ^4He . Its atomic mass can be determined in an experiment such as that illustrated in Figure 4-8. Modern mass spectrometers are capable of great accuracy in their mass measurements.

A beam of Ne^+ ions in the mass spectrometer is split into three segments. The mass spectrum of these ions (a graph of the relative numbers of ions of each mass) is shown in Figure 4-9. This indicates that neon occurs in nature as three isotopes: ^{20}Ne , ^{21}Ne , and ^{22}Ne . In Figure 4-9 we see that the isotope ^{20}Ne , mass 19.99244 amu, is the most abundant isotope (has the tallest peak). It accounts for 90.48% of the atoms. ^{22}Ne , mass 21.99138, accounts for 9.25%, and ^{21}Ne , mass 20.99384, for only 0.27% of the atoms.

Figure 4-10 shows a modern mass spectrometer. In nature, some elements, such as fluorine and phosphorus, exist in only one form, but most elements occur as isotopic mixtures. Some examples of natural isotopic abundances are given in Table 4-3. The percentages are based on the numbers of naturally occurring atoms of each isotope, not on their masses.

The distribution of isotopic masses, although nearly constant, does vary somewhat depending on the source of the element. For example, the abundance of ^{13}C in atmospheric CO_2 is slightly different from that in seashells. The chemical history of a sample can often be inferred from small differences in isotope ratios. See the Chemistry in Use essay on Stable Isotope Ratio Analysis.

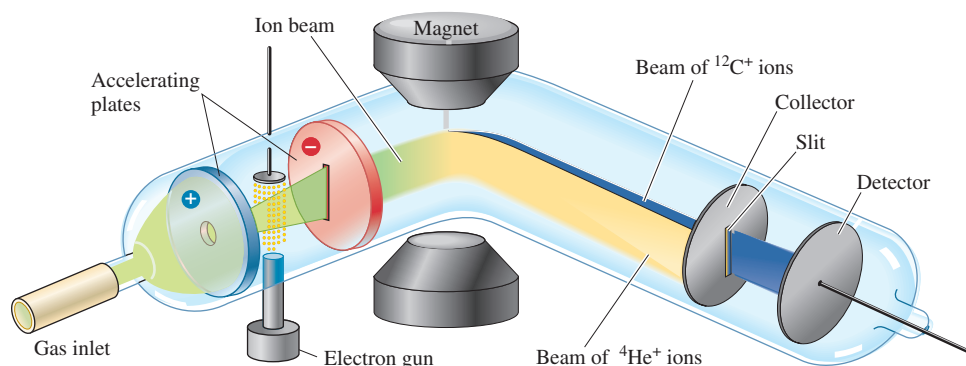


Figure 4-8 A mass spectrometer that uses a magnetic field to separate atoms or molecules with different masses. In this type of mass spectrometer, gas molecules at low pressure are ionized and accelerated by an electric field. The ion beam is then passed through a magnetic field. In that field the beam is resolved into components, each containing particles of equal charge-to-mass ratio. Lighter particles are deflected more strongly than heavy ones with the same charge. In a beam containing $^{12}\text{C}^+$ and $^4\text{He}^+$ ions, the lighter $^4\text{He}^+$ ions would be deflected more than the heavier $^{12}\text{C}^+$ ions. The spectrometer shown is adjusted to detect the $^{12}\text{C}^+$ ions. By changing the magnitude of the magnetic or electric field, we can move the beam of $^4\text{He}^+$ ions striking the collector so that it passes through the slit to reach the detector. The relative masses of the ions are calculated from the changes required to refocus the beam.

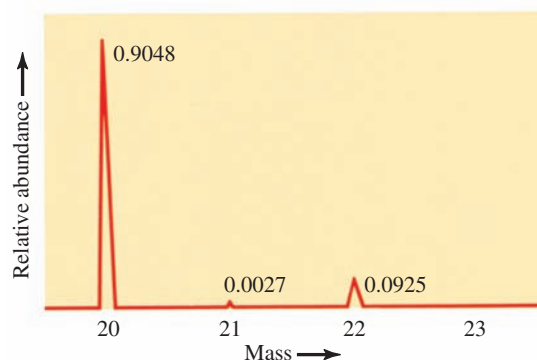


Figure 4-9 Mass spectrum of neon (1^+ ions only). Neon consists of three isotopes, of which neon-20 is by far the most abundant (90.48%). The mass of that isotope, to five decimal places, is 19.99244 amu on the carbon-12 (^{12}C) scale. The number by each peak corresponds to the fraction of all ions represented by the isotope with that mass.

► We can omit the atomic number subscript 2 for He, because all helium atoms have atomic number 2.

► Isotopes are two or more forms of atoms of the same element with different masses; the atoms contain the same number of protons but different numbers of neutrons.

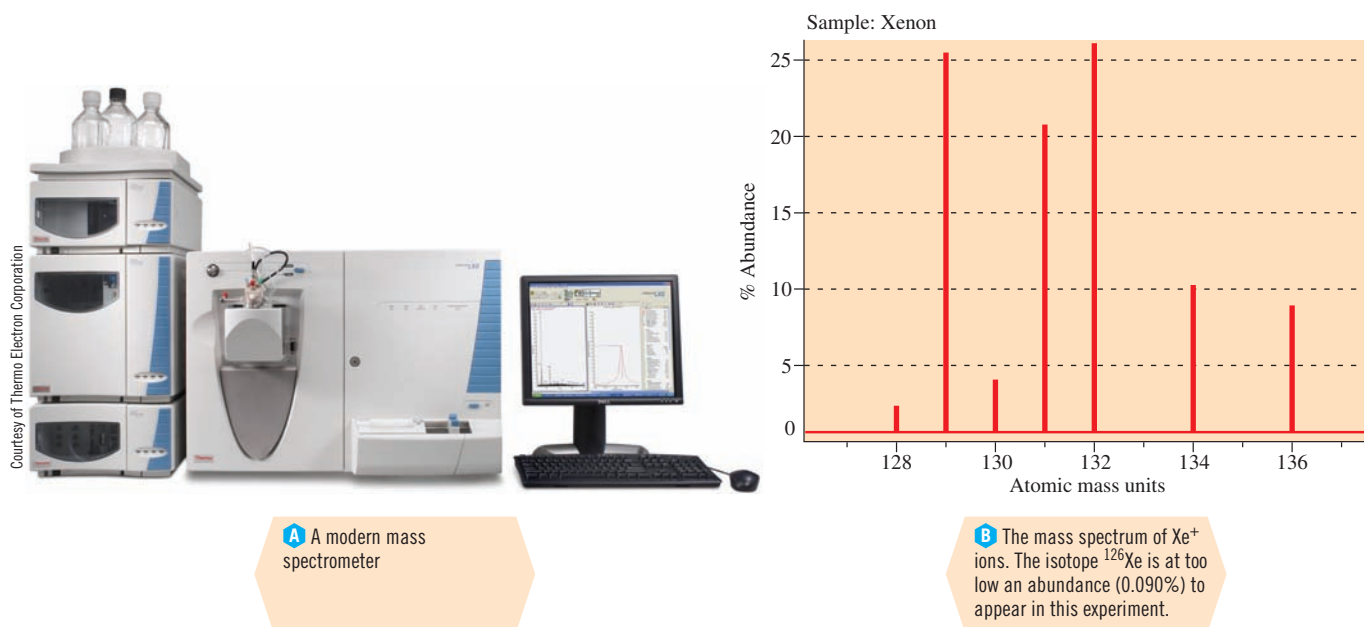


Figure 4-10 Mass spectrometer and mass spectrum of Xenon.

Table 4.3 Some Naturally Occurring Isotopic Abundances

Element	Atomic Weight (amu)	Isotope	% Natural Abundance	Mass (amu)
boron	10.81	^{10}B	19.91	10.01294
		^{11}B	80.09	11.00931
oxygen	15.999	^{16}O	99.762	15.99492
		^{17}O	0.038	16.99913
		^{18}O	0.200	17.99916
chlorine	35.45	^{35}Cl	75.770	34.96885
		^{37}Cl	24.230	36.96590
uranium	238.0289	^{234}U	0.0055	234.0409
		^{235}U	0.720	235.0439
		^{238}U	99.2745	238.0508

The 20 elements that have only one naturally occurring isotope are ^9Be , ^{19}F , ^{23}Na , ^{27}Al , ^{31}P , ^{45}Sc , ^{55}Mn , ^{59}Co , ^{75}As , ^{89}Y , ^{93}Nb , ^{103}Rh , ^{127}I , ^{133}Cs , ^{141}Pr , ^{159}Tb , ^{165}Ho , ^{169}Tm , ^{197}Au , and ^{209}Bi . There are, however, other artificially produced isotopes of these elements.

4-9 The Atomic Weight Scale and Atomic Weights

We learned in Section 2-4 that the *atomic weight scale* is based on the mass of the carbon-12 (^{12}C) isotope. As a result of action taken by the International Union of Pure and Applied Chemistry (IUPAC) in 1962,

► Described another way, the mass of one atom of ^{12}C is *exactly* 12 amu.

one **amu** is exactly 1/12 of the mass of a carbon-12 atom.

This is approximately the mass of one atom of ^1H , the lightest isotope of the element with lowest mass.

In Section 2-5 we saw that one mole of atoms contains 6.022×10^{23} atoms. The mass of one mole of atoms of any element, in grams, is numerically equal to the atomic weight of the element. Because the mass of one ^{12}C atom is exactly 12 amu, the mass of one mole of carbon-12 atoms is exactly 12 grams.

To show the relationship between atomic mass units and grams, let's calculate the mass, in amu, of 1.000 gram of ^{12}C atoms.

CHEMISTRY IN USE

Stable Isotope Ratio Analysis

Many elements exist as two or more stable isotopes, although one isotope is usually present in far greater abundance. For example, there are two stable isotopes of carbon, ^{13}C and ^{12}C of which ^{12}C is the more abundant, constituting 98.89% of all carbon. Similarly, there are two stable isotopes of nitrogen, ^{14}N and ^{15}N of which ^{14}N makes up 99.63% of all nitrogen.

Differences in chemical and physical properties that arise from differences in atomic mass of an element are known as isotope effects. We know that the extranuclear structure of an element (the number of electrons and their arrangement) essentially determines its chemical behavior, whereas the nucleus has more influence on many of the physical properties of the element. Because all isotopes of a given element contain the same number and arrangement of electrons, it was assumed for a long time that isotopes would behave identically in chemical reactions. In reality, although isotopes behave very similarly in chemical reactions, the correspondence is not perfect. The mass differences between different isotopes of the same element cause them to have slightly different physical and chemical properties. For example, the presence of only one additional neutron in the nucleus of the heavier isotope can cause it to react a little more slowly than its lighter counterpart. Such an effect often results in a ratio of heavy isotope to light isotope in the product of a reaction that is different from the ratio found in the reactant.

Stable isotope ratio analysis (SIRA) is an analytical method that takes advantage of the chemical and physical properties of isotopes as measured by isotope ratio mass spectrometry (IRMS). In this technique, the isotopic composition of a sample is measured using a mass spectrometer. This composition is then expressed as the relative ratios of two or more of the stable isotopes of a specific element. For instance, the ratio of ^{13}C to ^{12}C in a sample can be determined. This ratio is then compared with the isotope ratio of a defined standard. Because mass differences are most pronounced among the lightest elements, those elements experience the greatest isotope effects. Thus, the isotopes of the elements H, C, N, O, and S are used most frequently for SIRA. These elements have further significance because they are among the most abundant elements in biological systems.

The isotopic composition of a sample can be expressed as a “ δ ” value (δ), defined as

$$\delta X_{\text{sample}}(\text{‰}) = \frac{(R_{\text{sample}} - R_{\text{standard}})}{R_{\text{standard}}} \times 1000$$



Gerry Ellis/Digital Vision/Getty Images

where δX_{sample} is the isotope ratio relative to a standard, and R_{sample} and R_{standard} are the absolute isotope ratios of the sample and standard, respectively. Multiplying by 1000 allows the values to be expressed in parts per thousand (‰). If the δ value is a positive number, the sample has a greater amount of the heavier isotope than does the standard.

An interesting application of SIRA is the determination of the adulteration of food. As already mentioned, the isotope ratios of different plants and animals have been determined. For instance, corn has a $\delta^{13}\text{C}$ value of about -12‰ and most flowering plants have $\delta^{13}\text{C}$ values of about -26‰ . The difference in these $\delta^{13}\text{C}$ values arises because these plants carry out photosynthesis by slightly different chemical reactions. In the first reaction of photosynthesis, corn produces a molecule that contains four carbons, whereas flowering plants produce a molecule that has only three carbons. High-fructose corn syrup (HFCS) is thus derived from a “ C_4 ” plant, whereas the nectar that bees gather comes from “ C_3 ” plants. The slight differences in the photosynthetic pathways of C_3 and C_4 plants create the major differences in their $\delta^{13}\text{C}$ values. Brokers who buy and sell huge quantities of “sweet” products are able to monitor HFCS adulteration of honey, maple syrup, apple juice, and so on by taking advantage of the SIRA technique. If the $\delta^{13}\text{C}$ value of one of these products is not appropriate, then the product obviously has had other substances added to it; that is, it has been adulterated. The U.S. Department of Agriculture conducts routine isotope analyses to ensure the purity of those products submitted for subsidy programs. Similarly, the honey industry monitors itself with the SIRA approach.

Stable isotope ratio analysis is a powerful tool; many of its potential uses are now being recognized by researchers. Recent SIRA studies have included investigations of the geographical origins of olive oils and of cheeses from various localities, as well as the origins and dietary history of various meat sources such as beef, lamb, and fish. The use of stable isotope methods in research is becoming increasingly common, and through these methods scientists are attaining new levels of understanding of chemical, biological, and geological processes.

BETH A. TRUST

$$\begin{aligned} \underline{?} \text{ amu} &= 1.000 \text{ g } ^{12}\text{C atoms} \times \frac{1 \text{ mol } ^{12}\text{C}}{12 \text{ g } ^{12}\text{C atoms}} \times \frac{6.022 \times 10^{23} \text{ } ^{12}\text{C atoms}}{1 \text{ mol } ^{12}\text{C atoms}} \times \frac{12 \text{ amu}}{^{12}\text{C atom}} \\ &= 6.022 \times 10^{23} \text{ amu (in 1 g)} \end{aligned}$$

Thus,

$$1 \text{ g} = 6.022 \times 10^{23} \text{ amu} \quad \text{or} \quad 1 \text{ amu} = 1.660 \times 10^{-24} \text{ g}$$

► We saw in Chapter 2 that Avogadro's number is the number of particles of a substance in one mole of that substance. We now see that Avogadro's number also represents the number of amu in one gram. You may wish to verify that the same result is obtained regardless of the element or isotope chosen.

At this point, we emphasize the following:

1. The *atomic number*, Z , is an integer equal to the number of protons in the nucleus of an atom of the element. It is also equal to the number of electrons in a neutral atom. It is the same for all atoms of an element.
2. The *mass number*, A , is an integer equal to the *sum* of the number of protons and the number of neutrons in the nucleus of an atom of a *particular isotope* of an element. It is different for different isotopes of the same element.
3. Many elements occur in nature as mixtures of isotopes. The *atomic weight* of such an element is the weighted average of the masses of its isotopes. Atomic weights are fractional numbers, not integers.

The atomic weight that we determine experimentally (for an element that consists of more than one isotope) is such a weighted average. The following example shows how an atomic weight can be calculated from measured isotopic abundances.

EXAMPLE 4-2 Calculation of Atomic Weight

Three isotopes of magnesium occur in nature. Their abundances and masses, determined by mass spectrometry, are listed in the following table. Use this information to calculate the atomic weight of magnesium.

Isotope	% Abundance	Mass (amu)
^{24}Mg	78.99	23.98504
^{25}Mg	10.00	24.98584
^{26}Mg	11.01	25.98259

Plan

We multiply the fraction (percent divided by 100) of each isotope by its mass and add these numbers to obtain the atomic weight of magnesium.

Solution

$$\begin{aligned} \text{Atomic weight} &= 0.7899(23.98504 \text{ amu}) + 0.1000(24.98584 \text{ amu}) + 0.1101(25.98259 \text{ amu}) \\ &= 18.946 \text{ amu} \quad + 2.4986 \text{ amu} \quad + 2.8607 \text{ amu} \\ &= 24.30 \text{ amu} \quad (\text{to four significant figures}) \end{aligned}$$

You should now work Exercises 28 and 30.

STOP & THINK

The two heavier isotopes make small contributions to the atomic weight of magnesium because many more magnesium atoms are the lightest isotope, ^{24}Mg . Thus the atomic weight of magnesium is close to 24 amu.

Problem-Solving Tip “Weighted” Averages

Consider the following analogy to the calculation of atomic weights. Suppose you want to calculate the average weight of your classmates. Imagine that one-half of them weigh 100 pounds each, and the other half weigh 200 pounds each. The average weight would be

$$\text{Average weight} = \frac{1}{2}(100 \text{ lb}) + \frac{1}{2}(200 \text{ lb}) = 150 \text{ lb}$$

Imagine, however, that three-quarters of the class members weigh 100 pounds each, and the other quarter weigh 200 pounds each. Now, the average weight would be

$$\text{Average weight} = \frac{3}{4}(100 \text{ lb}) + \frac{1}{4}(200 \text{ lb}) = 125 \text{ lb}$$

We can express the fractions in this calculation in decimal form:

$$\text{Average weight} = 0.750(100 \text{ lb}) + 0.250(200 \text{ lb}) = 125 \text{ lb}$$

In such a calculation, the value (in this case, the weight) of each thing (people, atoms) is multiplied by the fraction of things that have that value. In Example 4-2 we expressed each percentage as a decimal fraction, such as

$$78.99\% = \frac{78.99 \text{ parts}}{100 \text{ parts total}} = 0.7899$$

Example 4-3 shows how the process can be reversed. Isotopic abundances can be calculated from isotopic masses and from the atomic weight of an element that occurs in nature as a mixture of only two isotopes.

EXAMPLE 4-3 Calculation of Isotopic Abundance

The atomic weight of gallium is 69.72 amu. The masses of the naturally occurring isotopes are 68.9257 amu for ^{69}Ga and 70.9249 amu for ^{71}Ga . Calculate the percent abundance of each isotope.

Plan

We represent the fraction of each isotope algebraically. Atomic weight is the weighted average of the masses of the constituent isotopes. So the fraction of each isotope is multiplied by its mass, and the sum of the results is equal to the atomic weight.

Solution

Let x = fraction of ^{69}Ga . Then $(1 - x)$ = fraction of ^{71}Ga .

$$x(68.9257 \text{ amu}) + (1 - x)(70.9249 \text{ amu}) = 69.72 \text{ amu}$$

$$68.9257x + 70.9249 - 70.9249x = 69.72$$

$$-1.9992x = -1.20$$

$$x = 0.600$$

$$x = 0.600 = \text{fraction of } ^{69}\text{Ga} \quad \therefore 60.0\% \text{ } ^{69}\text{Ga}$$

$$(1 - x) = 0.400 = \text{fraction of } ^{71}\text{Ga} \quad \therefore 40.0\% \text{ } ^{71}\text{Ga}$$

You should now work Exercise 32.

► When a quantity is represented by fractions, the sum of the fractions must always be one. In this case, $x + (1 - x) = 1$.

STOP & THINK

The observed atomic weight, 69.72, is closer to the mass of ^{69}Ga (68.9257) than to the other isotope. It is reasonable that there is more ^{69}Ga present (60.0%) than the heavier isotope, ^{71}Ga (40.0%).

4-10 The Periodic Table: Metals, Nonmetals, and Metalloids

In 1869, the Russian chemist Dmitri Mendeleev (1834–1907) and the German chemist Lothar Meyer (1830–1895) independently published arrangements of known elements that are much like the periodic table in use today. Mendeleev's classification was based primarily on chemical properties of the elements, whereas Meyer's classification was based largely on physical properties. The tabulations were surprisingly similar. Both emphasized the *periodicity*, or regular periodic repetition, of properties with increasing atomic weight.

Mendeleev arranged the known elements in order of increasing atomic weight in successive sequences so that elements with similar chemical properties fell into the same column. He

► When Mendeleev (pronounced “men-del-lay-ev”) and Meyer developed their tabulations, the concept of atomic number was not yet known. Their classifications were based on the atomic weights known at that time.

Unless otherwise noted, all content on this page is © Cengage Learning.



Not all properties of the elements can be predicted from the trends in the periodic table. For example, gallium's melting point being low enough to melt from the heat of the hand is inconsistent with the properties of the elements above and below it.

noted that both physical and chemical properties of the elements vary in a periodic fashion with atomic weight. His periodic table of 1872 contained the 62 known elements (Figure 4-11). Mendeleev placed H, Li, Na, and K in his table as “Gruppe I.” These were known to combine with F, Cl, Br, and I of “Gruppe VII” to produce compounds that have similar formulas such as HF, LiCl, NaCl, and KI. All these compounds dissolve in water to produce solutions that conduct electricity. The “Gruppe II” elements were known to form compounds such as BeCl₂, MgBr₂, and CaCl₂, as well as compounds with O and S from “Gruppe VI” such as MgO, CaO, MgS, and CaS. These and other chemical properties led him to devise a table in which the elements were arranged by increasing atomic weights and grouped into vertical families.

In most areas of human endeavor progress is slow and faltering. Occasionally, however, an individual develops concepts and techniques that clarify confused situations. Mendeleev was such an individual. One of the brilliant successes of his periodic table was that it provided for elements that were unknown at the time. When he encountered “missing”

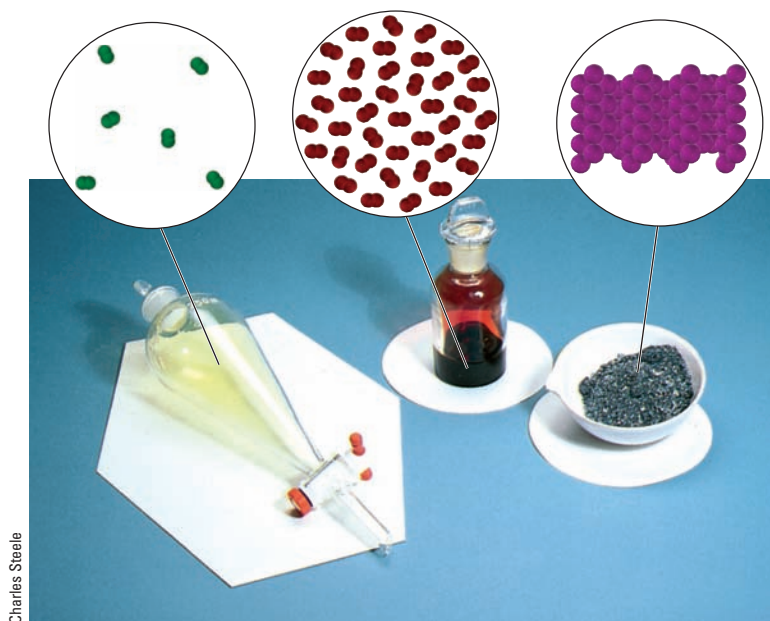
REIHEN	GRUPPE I — R ² O	GRUPPE II — RO	GRUPPE III — R ² O ³	GRUPPE IV RH ⁴ RO ²	GRUPPE V RH ³ R ² O ⁵	GRUPPE VI RH ² RO ³	GRUPPE VII RH R ² O ⁷	GRUPPE VIII — RO ⁴
1	H = 1							
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199.
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

Figure 4-11 Mendeleev's early periodic table (1872). “J” is the German symbol for iodine.

Lithium (top left) and sodium (bottom left) from Group 1A. Magnesium (top right) and calcium (bottom right) from Group 2A.

Charles D. Winters

elements, Mendeleev left blank spaces. Some appreciation of his genius in constructing the table as he did can be gained by comparing the predicted (1871) and observed properties of germanium, which was not discovered until 1886. Mendeleev called the undiscovered element eka-silicon (Es) because it fell below silicon in his table. He was familiar with the properties of germanium's neighboring elements. They served as the basis for his predictions of properties of germanium (Table 4-4). Some modern values for the properties of germanium differ significantly from those reported in 1886. But many of the values on which Mendeleev based his predictions were also inaccurate.



Three of the halogens, elements from Group 7A (left to right): chlorine, bromine, iodine.

Table 4-4 Predicted and Observed Properties of Germanium

Property	Eka-Silicon Predicted, 1871	Germanium Reported, 1886	Modern Values
Atomic weight	72	72.32	72.61
Atomic volume	13 cm ³ /mol	13.22 cm ³ /mol	13.5 cm ³ /mol
Specific gravity	5.5	5.47	5.35
Specific heat	0.073 cal/g°C	0.076 cal/g°C	0.074 cal/g°C
Maximum valence*	4	4	4
Color	Dark gray	Grayish white	Grayish white
Reaction with water	Will decompose steam with difficulty	Does not decompose water	Does not decompose water
Reactions with acids and alkalis	Slight with acids; more pronounced with alkalis	Not attacked by HCl or dilute aqueous NaOH; reacts vigorously with molten NaOH	Not dissolved by HCl or H ₂ SO ₄ or dilute NaOH; dissolved by concentrated NaOH
Formula of oxide	EsO ₂	GeO ₂	GeO ₂
Specific gravity of oxide	4.7	4.703	4.228
Specific gravity of tetrachloride	1.9 at 0°C	1.887 at 18°C	1.8443 at 30°C
Boiling point of tetrachloride	100°C	86°C	84°C
Boiling point of tetraethyl derivative	160°C	160°C	186°C

*"Valence" refers to the combining power of a specific element.

Unless otherwise noted, all content on this page is © Cengage Learning.

Because Mendeleev's arrangement of the elements was based on increasing *atomic weights*, several elements would have been out of place in his table. Mendeleev put the controversial elements (Te and I, Co and Ni) in locations consistent with their properties, however. He thought the apparent reversal of atomic weights was due to inaccurate values for those weights. Careful redetermination showed that the values were correct. Explanation of the locations of these “out-of-place” elements had to await the development of the concept of *atomic number*, approximately 50 years after Mendeleev's work. The **atomic number** (see Section 4-5) of an element is the number of protons in the nucleus of its atoms. (It is also the number of electrons in a neutral atom of an element.) This quantity is fundamental to the identity of each element. Elements are now arranged in the periodic table in order of increasing atomic number. With the development of this concept, the **periodic law** attained its present form:

The properties of the elements are periodic functions of their atomic numbers.

The periodic law tells us that if we arrange the elements in order of increasing atomic number, we periodically encounter elements that have similar chemical and physical properties. The presently used “long form” of the periodic table (Table 4-5 and inside the front cover) is such an arrangement. The vertical columns are referred to as **groups** or **families**, and the horizontal rows are called **periods**. Elements in a *group* have similar chemical and physical properties, and those within a *period* have properties that change progressively across the table. Several groups of elements have common names that are used so frequently they should be learned. The Group 1A elements, except H, are referred to as **alkali metals**, and the Group 2A elements are called the **alkaline earth metals**.

► Alkaline means basic. The character of basic compounds is described in Section 10-4.

Table 4-5 The Periodic Table

Alkali metals			Metals										Noble gases					
1A Alkaline earth metals			Nonmetals										8A (18)					
(1)													Halogens					
1	1 H	2A (2)											3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	2 He
2	3 Li	4 Be	Transition metals										5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8) (9) (10)			1B (11)	2B (12)	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 (Uut)	114 Fl	115 (Uup)	116 Lv	117 (Uus)	118 (Uuo)
				* 58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu														
				† 90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No 103 Lr														

There are other systems for numbering the groups in the periodic table. We number the groups by the standard American system of A and B groups. An alternative system, recommended by IUPAC, in which the groups are numbered 1 through 18 is shown in parentheses.

Unless otherwise noted, all content on this page is © Cengage Learning.

The Group 7A elements are called **halogens**, which means “salt formers,” and the Group 8A elements are called **noble** (or **rare**) **gases**.

The general properties of metals and nonmetals are distinct. Physical and chemical properties that distinguish metals from nonmetals are summarized in Tables 4-6 and 4-7. Not all metals and nonmetals possess all these properties, but they share most of them to varying degrees. The physical properties of metals can be explained on the basis of metallic bonding in solids (see Section 13-17).

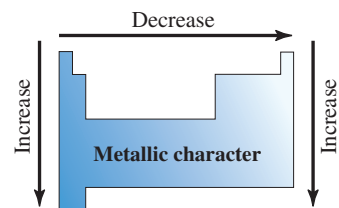
Table 4-5, The Periodic Table, shows how we classify the known elements as **metals** (shown in blue), **nonmetals** (tan), and **metalloids** (green). The elements to the left of those touching the heavy stairstep line are metals (except hydrogen), and those to the right are nonmetals. Such a classification is somewhat arbitrary, and several elements do not fit neatly into either class. Most elements adjacent to the heavy line are often called **metalloids** (or semimetals), because they are metallic (or nonmetallic) only to a limited degree.

Metallic character increases from top to bottom and decreases from left to right with respect to position in the periodic table.

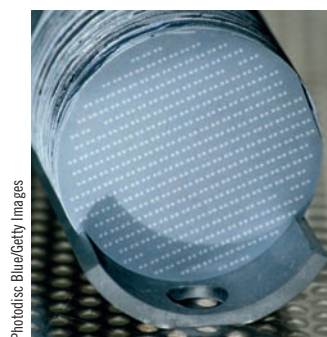
Cesium, atomic number 55, is the most active naturally occurring metal. Francium and radium are radioactive and do not occur in nature in appreciable amounts. Noble gases seldom bond with other elements. They are unreactive, monatomic gases. The most active nonmetal is fluorine, atomic number 9.

Nonmetallic character decreases from top to bottom and increases from left to right in the periodic table.

▶ About 80% of the elements are metals.



General trends in metallic character of A group elements with position in the periodic table.



Silicon, a metalloid, is widely used in the manufacture of electronic chips.

Table 4-6 Some Physical Properties of Metals and Nonmetals

Metals	Nonmetals
1. High electrical conductivity that decreases with increasing temperature 2. High thermal conductivity 3. Metallic gray or silver luster* 4. Almost all are solids† 5. Malleable (can be hammered into sheets) 6. Ductile (can be drawn into wires)	1. Poor electrical conductivity (except carbon in the form of graphite) 2. Good heat insulators (except carbon) 3. No metallic luster 4. Solids, liquids, or gases 5. Brittle in solid state 6. Nonductile

*Except copper and gold.

†Except mercury; cesium and gallium melt at body temperature (37°C).

Table 4-7 Some Chemical Properties of Metals and Nonmetals

Metals	Nonmetals
1. Outer shells contain few electrons—usually three or fewer 2. Form cations (positive ions) by losing electrons 3. Form ionic compounds with nonmetals 4. Solid state characterized by metallic bonding	1. Outer shells contain four or more electrons* 2. Form anions (negative ions) by gaining electrons† 3. Form ionic compounds with metals† and molecular (covalent) compounds with nonmetals 4. Covalently bonded molecules; noble gases are monatomic

*Except hydrogen and helium.

†Except the noble gases.

► Aluminum is the most abundant metal in the earth's crust (7.5% by mass).

Metalloids show some properties that are characteristic of both metals and nonmetals. Many of the metalloids, such as silicon, germanium, and antimony, act as semiconductors, which are important in solid-state electronic circuits. **Semiconductors** are insulators at lower temperatures but become conductors at higher temperatures (see Section 13-17). The conductivities of metals, by contrast, decrease with increasing temperature.

Aluminum is the least metallic of the metals and is sometimes classified as a metalloid. It is metallic in appearance and an excellent conductor of electricity.

In later chapters we will study some chemical reactions of elements and their compounds and relate the reactions to the locations of the elements in the periodic table. First, we will describe the arrangements of electrons in atoms. A knowledge of these arrangements not only provides the physical basis for the periodic table, but also explains chemical bonding and properties.

The Electronic Structures of Atoms

The Rutherford model of the atom is consistent with the evidence presented so far, but it has some serious limitations. It does not answer such important questions as: *Why* do different elements have such different chemical and physical properties? *Why* do chemical and physical properties fall into the regular patterns summarized by the periodic table? *Why* does chemical bonding occur? *Why* does each element form compounds with characteristic formulas? *How* can atoms of different elements give off or absorb light only of characteristic colors (as was known long before 1900)?

To improve our understanding, we must first learn more about the arrangements of electrons in atoms. The theory of these arrangements is based largely on the study of the light given off and absorbed by atoms. Then we will develop a detailed picture of the *electron configurations* of different elements. A knowledge of these arrangements will help us to understand the periodic table and chemical bonding.

4-11 Electromagnetic Radiation

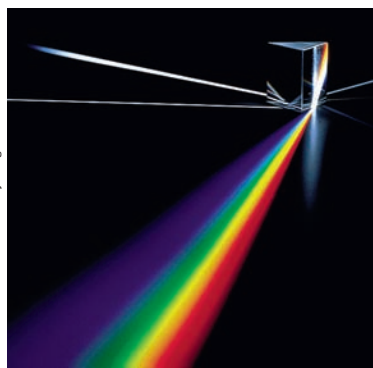
Our ideas about the arrangements of electrons in atoms have evolved slowly. Much information has been derived from atomic **emission spectra**. These are the bright lines, or bands, produced on photographic film by radiation that has passed through a refracting glass prism after being emitted from electrically or thermally excited atoms. To help us understand the nature of atomic spectra, we first describe electromagnetic radiation.

All types of electromagnetic radiation, or radiant energy, can be described in the terminology of waves. To help characterize any wave, we specify its *wavelength* (or its *frequency*). Let's use a familiar kind of wave, that on the surface of water (Figure 4-12), to illustrate these terms. The significant feature of wave motion is its repetitive nature. The **wavelength**, λ (Greek letter "lambda"), is the distance between any two adjacent identical points of the wave, for instance, two adjacent crests. The **frequency** is the number of wave crests passing a given point per unit time; it is represented by the symbol ν (Greek letter "nu") and is usually expressed in cycles per second or, more commonly, simply as $1/s$ or s^{-1} with "cycles" understood. For a wave that is "traveling" at some speed, the wavelength and the frequency are related to each other by

$$\lambda\nu = \text{speed of propagation of the wave} \quad \text{or} \quad \lambda\nu = c \text{ (for light)} \quad \text{or} \quad \lambda\nu = v \text{ (for all other waves)}$$

Thus, wavelength and frequency are inversely proportional to each other; for the same wave speed, shorter wavelengths correspond to higher frequencies.

For water waves, it is the surface of the water that changes repetitively; for a vibrating violin string, it is the displacement of any point on the string. Electromagnetic radiation is a form of energy that consists of electric and magnetic fields that vary repetitively (Figure 4-13).



White light is dispersed by a prism into a *continuous spectrum*.

► One cycle per second is also called one *hertz* (Hz), after Heinrich Hertz (1857–1894). In about 1887, Hertz discovered electromagnetic radiation outside the visible range and measured its speed and wavelengths.



The diffraction of white light by the closely spaced grooves of a compact disk spreads the light into its component colors. Diffraction is due to the constructive and destructive interference of light waves.

Unless otherwise noted, all content on this page is © Cengage Learning.

The electromagnetic radiation most obvious to us is visible light. It has wavelengths ranging from about 4.0×10^{-7} m (violet) to about 7.5×10^{-7} m (red). Expressed in frequencies, this range is about 7.5×10^{14} Hz (violet) to about 4.0×10^{14} Hz (red).

Isaac Newton (1642–1727) first recorded the separation of sunlight into its component colors by allowing it to pass through a glass prism. Because sunlight (white light) contains all wavelengths of visible light, it gives the **continuous spectrum** observed in a rainbow (Figure 4-14a). But visible light represents only a tiny segment of the electromagnetic radiation spectrum (Figure 4-14b). In addition to all wavelengths of visible light, sunlight also contains shorter wavelength (ultraviolet) radiation as well as longer wavelength (infrared) radiation. Neither ultraviolet nor infrared radiation can be detected by the human eye. Both may be detected and recorded photographically or by detectors designed for that purpose. Many other familiar kinds of radiation are simply electromagnetic radiation of longer or shorter wavelengths.

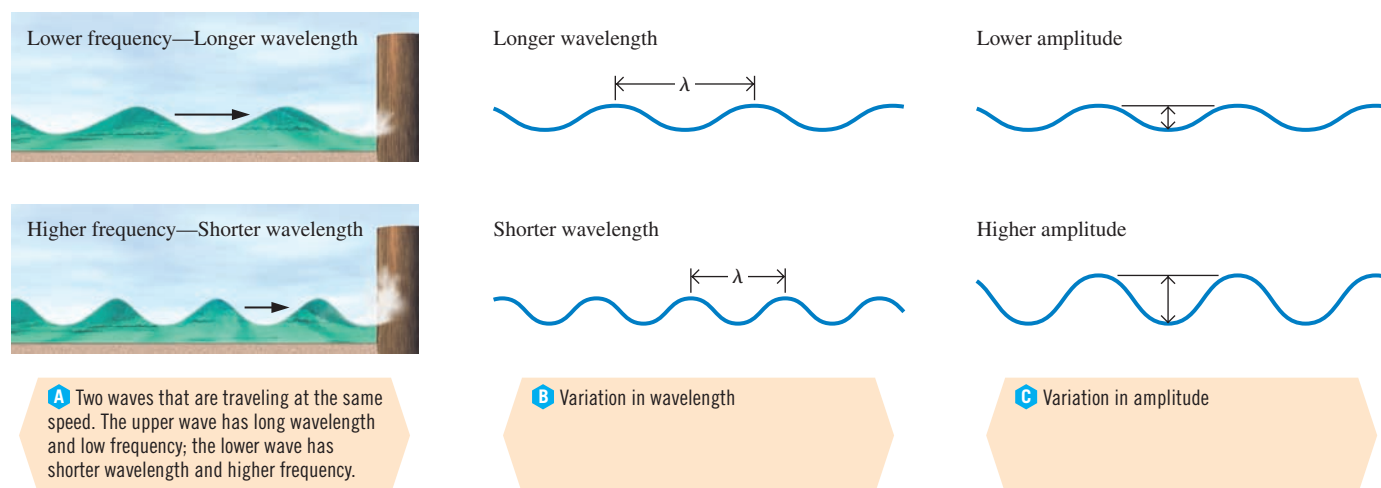


Figure 4-12 Illustrations of the wavelength and frequency of water waves. The distance between any two identical points, such as crests, is the wavelength, λ . We could measure the frequency, ν , of the wave by observing how often the level rises and falls at a fixed point in its path—for instance, at the post—or how often crests hit the post.

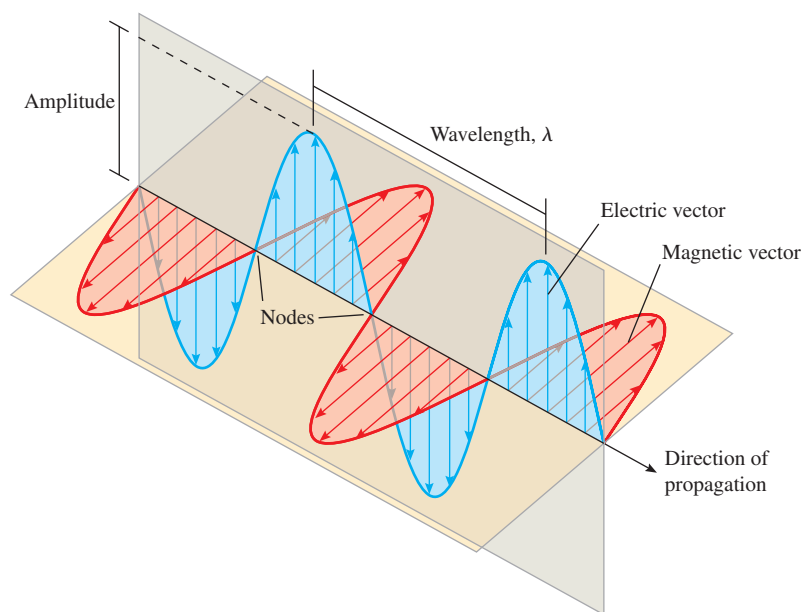
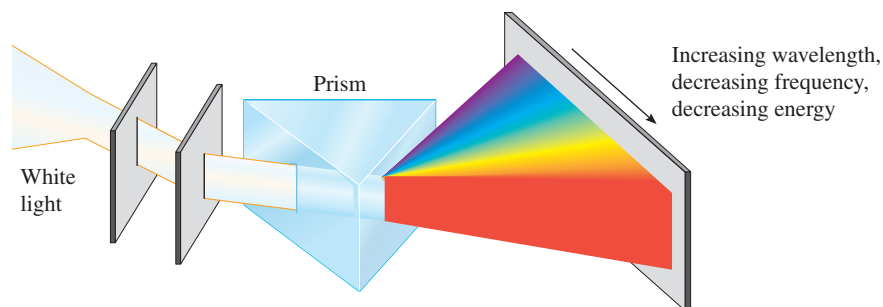
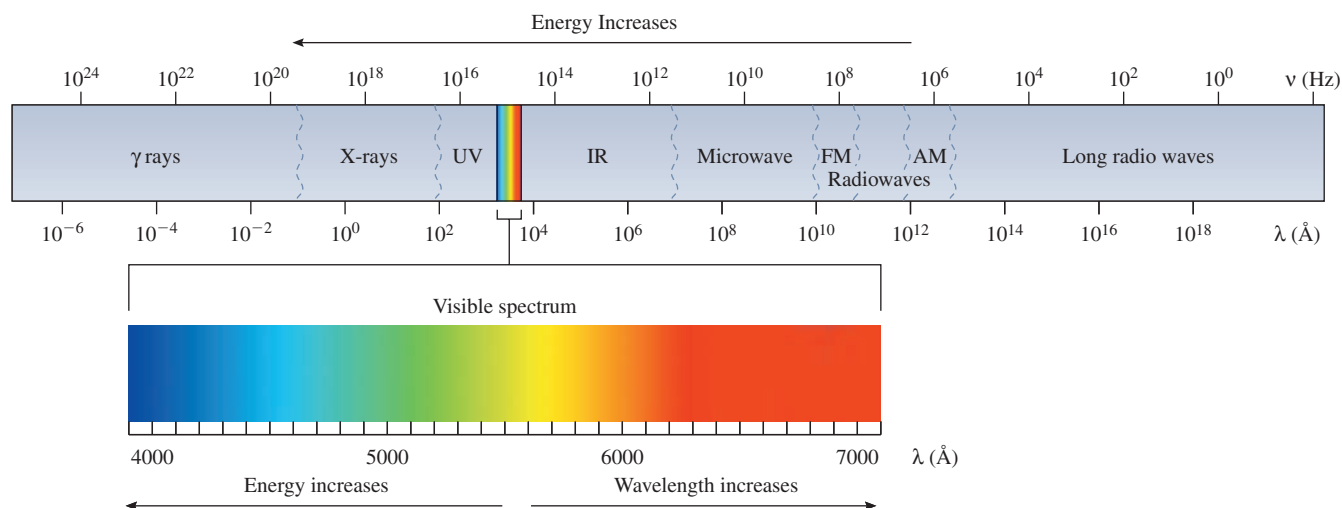


Figure 4-13 All forms of radiation, including visible light, consist of electric and magnetic fields that vary repetitively at right angles to each other. A more intense beam corresponds to a higher amplitude of electric and magnetic fields. This combination of waves moves in the direction of travel of the light beam, similar to the motion of the water waves in Figure 4-12.

Unless otherwise noted, all content on this page is © Cengage Learning.



A Dispersion of visible light by a prism. Light from a source of white light is passed through a slit and then through a prism. It is spread into a continuous spectrum of all wavelengths of visible light.



B Visible light is only a very small portion of the electromagnetic spectrum. Most electromagnetic radiation has longer or shorter wavelengths than our eyes can detect. The approximate ranges of the electromagnetic spectrum are shown on a logarithmic scale. The visible region is shown on an expanded scale. Note that wavelength increases as frequency decreases.

Figure 4-14 The electromagnetic spectrum.

In a vacuum, the speed of electromagnetic radiation, c , is the same for all wavelengths, 2.99792458×10^8 m/s. The relationship between the wavelength and frequency of electromagnetic radiation, with c rounded to three significant figures, is

$$\lambda\nu = c = 3.00 \times 10^8 \text{ m/s (or 186,000 miles/s)}$$

EXAMPLE 4-4 Wavelength of Light

Light near the middle of the ultraviolet region of the electromagnetic radiation spectrum has a frequency of $2.73 \times 10^{16} \text{ s}^{-1}$. Yellow light near the middle of the visible region of the spectrum has a frequency of $5.26 \times 10^{14} \text{ s}^{-1}$. Calculate the wavelength that corresponds to each of these two frequencies of light.

Plan

Wavelength and frequency are inversely proportional to each other, $\lambda\nu = c$. We solve this relationship for λ and calculate the wavelengths.



Sir Isaac Newton, one of the giants of science. You probably know of him from his theory of gravitation. In addition, he made enormous contributions to the understanding of many other aspects of physics, including the nature and behavior of light, optics, and the laws of motion. He is credited with the invention of differential calculus and of expansions into infinite series.

Unless otherwise noted, all content on this page is © Cengage Learning.

Solution

$$\text{(ultraviolet light)} \quad \lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{2.73 \times 10^{16} \text{ s}^{-1}} = 1.10 \times 10^{-8} \text{ m } (1.10 \times 10^2 \text{ \AA})$$

$$\text{(yellow light)} \quad \lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{5.26 \times 10^{14} \text{ s}^{-1}} = 5.70 \times 10^{-7} \text{ m } (5.70 \times 10^3 \text{ \AA})$$

You should now work Exercise 54.

STOP & THINK

Wavelength and frequency are inversely proportional to one another. Thus the radiation with the higher frequency (ultraviolet) has the shorter wavelength.

We have described light in terms of wave behavior. Under certain conditions, it is also possible to describe light as composed of *particles*, or **photons**. According to the ideas presented by Max Planck (1858–1947) in 1900, each photon of light corresponds to a particular amount (a **quantum**) of energy. The energy of a photon depends on the frequency of the light. The energy of a photon of light is given by Planck's equation

$$E = h\nu \quad \text{or} \quad E = \frac{hc}{\lambda}$$

where h is Planck's constant, $6.62606896 \times 10^{-34} \text{ J} \cdot \text{s}$, and ν is the frequency of the light. Thus, energy is directly proportional to frequency. Planck's equation is used in Example 4-5 to show that a photon of ultraviolet light has more energy than a photon of yellow light.

EXAMPLE 4-5 Energy of Light

In Example 4-4 we calculated the wavelengths of ultraviolet light of frequency $2.73 \times 10^{16} \text{ s}^{-1}$ and of yellow light of frequency $5.26 \times 10^{14} \text{ s}^{-1}$. Calculate the energy, in joules, of an individual photon of each. Compare these photons by calculating the ratio of their energies.

Plan

We use each frequency to calculate the photon energy from the relationship $E = h\nu$. Then we calculate the required ratio.

Solution

$$\text{(ultraviolet light)} \quad E = h\nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.73 \times 10^{16} \text{ s}^{-1}) = 1.81 \times 10^{-17} \text{ J}$$

$$\text{(yellow light)} \quad E = h\nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(5.26 \times 10^{14} \text{ s}^{-1}) = 3.49 \times 10^{-19} \text{ J}$$

(You can check these answers by calculating the energies directly from the wavelengths, using the equation $E = hc/\lambda$.)

Now, we compare the energies of these two photons.

$$\frac{E_{\text{uv}}}{E_{\text{yellow}}} = \frac{1.81 \times 10^{-17} \text{ J}}{3.49 \times 10^{-19} \text{ J}} = 51.9$$

A photon of light near the middle of the ultraviolet region is more than 51 times as energetic than a photon of light near the middle of the visible region. Photon energy is proportional to frequency, so the light with highest frequency (ultraviolet) has the highest photon energy.

You should now work Exercise 55.

► This is one reason why ultraviolet (UV) light damages your skin much more rapidly than visible light. Another reason is that many of the organic compounds in the skin absorb UV light more readily than visible light. For many biologically important molecules, a single photon of ultraviolet light is enough energy to break a chemical bond, often producing very reactive and damaging molecular fragments.

Unless otherwise noted, all content on this page is © Cengage Learning.

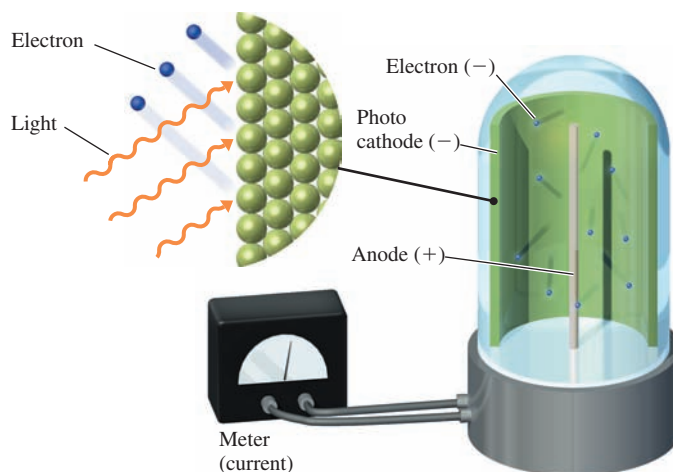


Figure 4-15 The photoelectric effect. When electromagnetic radiation of sufficient minimum energy strikes the surface of a metal (negative electrode or cathode) inside an evacuated tube, electrons are stripped off the metal to create an electric current. The current increases with increasing radiation intensity.

4-12 The Photoelectric Effect

One phenomenon that had not been satisfactorily explained with the wave theory of light was the **photoelectric effect**. The apparatus for the photoelectric effect is shown in Figure 4-15. The negative electrode (cathode) in the evacuated tube is made of a pure metal such as cesium. When light of a sufficiently high energy strikes the metal, electrons are knocked off its surface. They then travel to the positive electrode (anode) to produce a current flowing through the circuit. The important observations follow.

1. Electrons are ejected only if the light is of sufficiently short wavelength (has sufficiently high energy), no matter how long or how brightly the light shines. This wavelength limit is different for different metals.
2. If the photon energy of the light is high enough to start the photoelectric effect, the number of electrons emitted per second (the current) increases as the brightness (intensity) of the light increases. The amount of current does not depend on the wavelength (color) of the light used after the minimum photon energy needed to initiate the photoelectric effect is reached.

Classical theory said that even “low-” energy light should cause current to flow if the metal is irradiated long enough. Electrons should accumulate energy and be released when they have enough energy to escape from the metal atoms. According to the old theory, if the light is made more energetic, then the current should increase even though the light intensity remains the same. Such is *not* the case.

The answer to the puzzle was provided by Albert Einstein (1879–1955). In 1905 he extended Planck’s idea that light behaves as though it were composed of *photons*, each with a particular amount (a quantum) of energy. According to Einstein, each photon can transfer all of its energy to a single electron during a collision. When we say that the intensity of light is increased, we mean that the number of photons striking a given area per second is increased. The picture is now one of a particle of light striking an electron near the surface of the metal and giving up its energy to the electron. If that energy is equal to or greater than the amount needed to liberate the electron, it can escape to join the photoelectric current. For this explanation, Einstein received the 1921 Nobel Prize in Physics.

4-13 Atomic Spectra and the Bohr Atom

Incandescent (“red hot” or “white hot”) solids, liquids, and high-pressure gases give continuous spectra. When an electric current is passed through a gas in a vacuum tube at very low pressures, however, the light that the gas emits can be dispersed by a prism into dis-

► The intensity of light is the brightness of the light. In wave terms, it is related to the amplitude of the light waves. In photon terms, it is the number of photons hitting the target.



The sensor for each “pixel” in a digital camera is a tiny photoelectric device. The photoelectric sensors that open some supermarket and elevator doors also utilize this effect.

tinct lines (Figure 4-16a). The resulting **emission spectrum** is described as a *bright line spectrum*. The lines can be recorded photographically, and the wavelength of light that produced each line can be calculated from the position of that line on the photograph.

Similarly, we can shine a beam of white light (containing a continuous distribution of wavelengths) through a gas and analyze the beam that emerges. We find that only certain wavelengths have been absorbed (Figure 4-16b). The wavelengths that are absorbed in this **absorption spectrum** are the same as those given off in the emission experiment. Each spectral line corresponds to a specific wavelength of light and thus to a specific amount of energy that is either absorbed or emitted. Each element displays its own characteristic set of lines in its emission or absorption spectrum (Figure 4-17). These spectra can serve as “fingerprints” that allow us to identify different elements present in a sample, even in trace amounts.

EXAMPLE 4-6 Energy of Light

A green line of wavelength 4.86×10^{-7} m is observed in the emission spectrum of hydrogen. Calculate the energy of one photon of this green light.

Plan

We know the wavelength of the light, and we calculate its frequency so that we can then calculate the energy of each photon.

Solution

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(4.86 \times 10^{-7} \text{ m})} = 4.09 \times 10^{-19} \text{ J/photon}$$

To gain a better appreciation of the amount of energy involved, let's calculate the total energy, in kilojoules, emitted by one mole of atoms. (Each atom emits one photon.)

$$\frac{? \text{ kJ}}{\text{mol}} = 4.09 \times 10^{-19} \frac{\text{J}}{\text{atom}} \times \frac{1 \text{ kJ}}{1 \times 10^3 \text{ J}} \times \frac{6.02 \times 10^{23} \text{ atoms}}{\text{mol}} = 2.46 \times 10^2 \text{ kJ/mol}$$

This calculation shows that when each atom in one mole of hydrogen atoms emits light of wavelength 4.86×10^{-7} m, the mole of atoms loses 246 kJ of energy as green light. (This would be enough energy to operate a 100-watt light bulb for more than 40 minutes.)

You should now work Exercises 56 and 58.

STOP & THINK

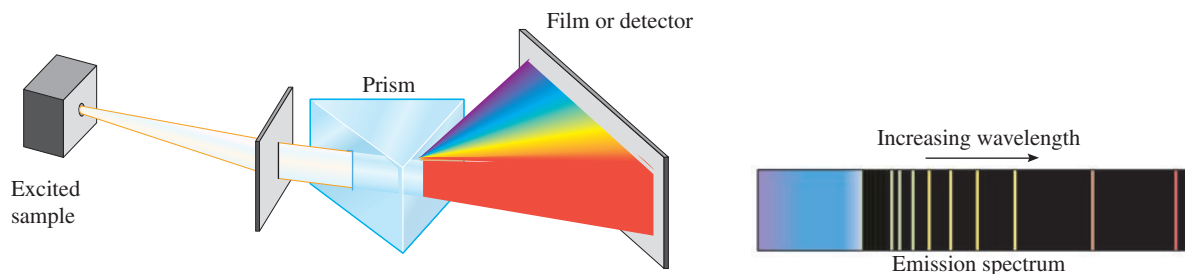
Be careful of unit conversions in calculations such as this.

When an electric current is passed through hydrogen gas at very low pressures, several series of lines in the spectrum of hydrogen are produced. These lines were studied intensely by many scientists. In the late 19th century, Johann Balmer (1825–1898) and Johannes Rydberg (1854–1919) showed that the wavelengths of the various lines in the hydrogen spectrum can be related by a mathematical equation:

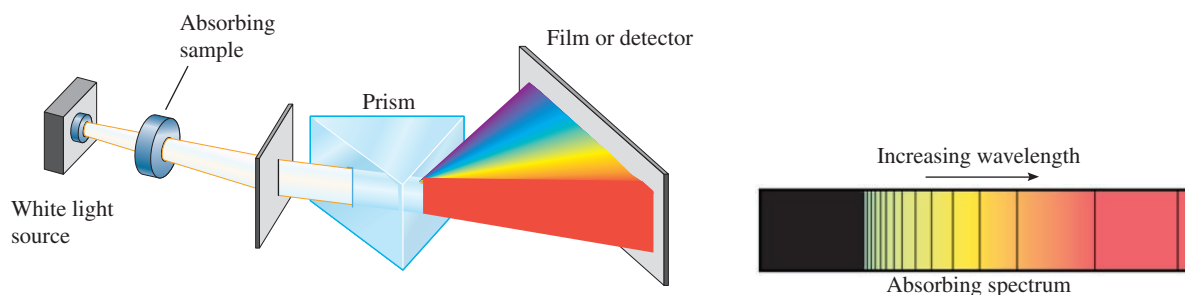
$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Here R is $1.097 \times 10^7 \text{ m}^{-1}$ and is known as the Rydberg constant. The n 's are positive integers, and n_1 is smaller than n_2 . The Balmer–Rydberg equation was derived from numerous observations, not from theory. It is thus an empirical equation.

In 1913 Niels Bohr (1885–1962), a Danish physicist, provided an explanation for Balmer and Rydberg's observations. He wrote equations that described the electron of a hydrogen atom as revolving around its nucleus in one of a discrete set of circular orbits. He added the condition that the electronic energy is *quantized*; that is, only certain values of electronic energy are possible. This led him to suggest that electrons can only be in certain discrete orbits, and that they absorb or emit energy in discrete

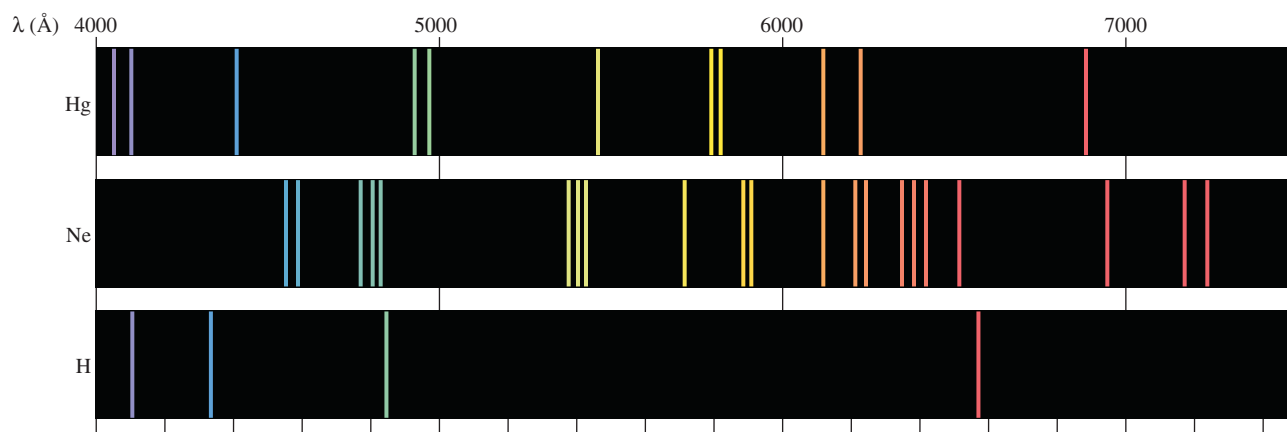


A Atomic emission. The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into discrete wavelengths. Thus, an emission spectrum, which is a photographic recording of the separated wavelengths, is called a line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains many possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum.

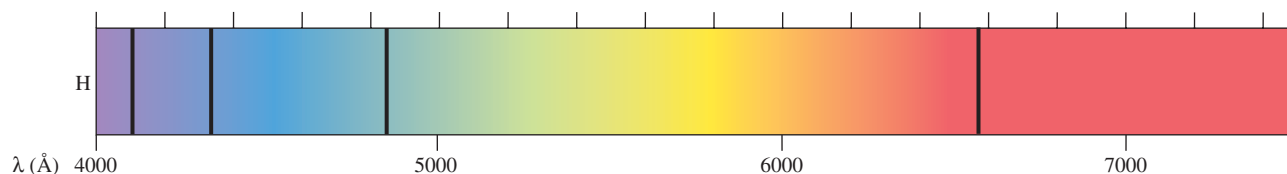


B Atomic absorption. When white light is passed through unexcited hydrogen and then through a slit and a prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in part (a). The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.

Figure 4-16

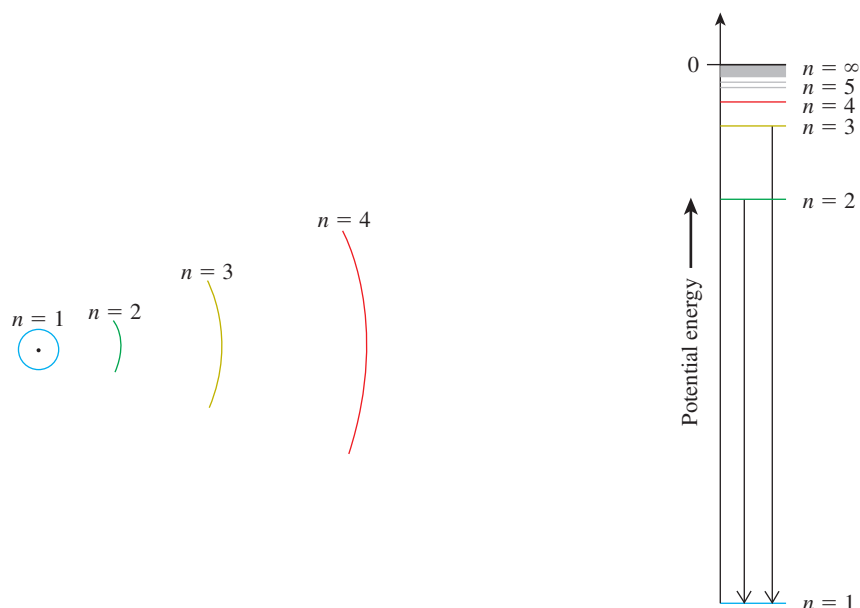


A Emission spectra for some elements



B Absorption spectrum for hydrogen. Compare the positions of these lines with those in the emission spectrum for H in (a).

Figure 4-17 Atomic spectra in the visible region for some elements. Figure 4-16 shows how such spectra are produced.



A The radii of the first four Bohr orbits for a hydrogen atom. The dot at the center represents the nuclear position. The radius of each orbit is proportional to n^2 , so the orbits are more widely spaced as the n value increases. These four radii are in the ratio 1:4:9:16.

B Relative values for the energies associated with some Bohr energy levels in a hydrogen atom. By convention, the potential energy of the electron is defined as zero when it is at an infinite distance from the nucleus. Any more stable arrangement would have a lower potential energy. The energy spacing between orbits gets smaller as the n value increases. For very large values of n , the energy levels are so close together that they form a continuum. Some possible electronic transitions corresponding to lines in the hydrogen emission spectrum are indicated by arrows. Transitions in the opposite direction account for lines in the absorption spectrum. The biggest energy *change* occurs when an electron jumps between $n = 1$ and $n = 2$; a considerably smaller energy change occurs when the electron jumps between $n = 3$ and $n = 4$.



The lightning flashes produced in electrical storms and the light produced by neon gas in neon signs are two familiar examples of visible light produced by electronic transitions.

STOP & THINK
Remember that the orbits get farther apart as n increases, but their energies get closer together.

Figure 4-18

amounts as they move from one orbit to another. Each orbit thus corresponds to a definite *energy level* for the electron. When an electron is excited from a lower energy level to a higher one, it absorbs a definite (quantized) amount of energy. When the electron falls back to the original energy level, it emits exactly the same amount of energy that it absorbed in moving from the lower to the higher energy level. Figure 4-18 illustrates these transitions schematically. The values of n_1 and n_2 in the Balmer–Rydberg equation identify the lower and higher levels, respectively, of these electronic transitions.

ENRICHMENT

The Bohr Theory and the Balmer–Rydberg Equation

From mathematical equations describing the orbits for the hydrogen atom, together with the assumption of quantization of energy, Bohr was able to determine two significant aspects of each allowed orbit:

1. *Where* the electron can be with respect to the nucleus—that is, the radius, r , of the circular orbit. This is given by

$$r = n^2 a_0$$

► *Note:* r is proportional to n^2 . Higher values of n correspond to larger r , with the electron farther from the nucleus.

► *Note:* E is proportional to $-\frac{1}{n^2}$.

Higher values of n correspond to higher (less negative) energies, with the electron less stable.

► We define the potential energy of a set of charged particles to be zero when the particles are infinitely far apart.

where n is a positive integer (1, 2, 3, ...) that tells which orbit is being described and a_0 is the *Bohr radius*. Using a combination of Planck's constant, the charge of the electron, and the mass of the electron, Bohr was able to calculate the value of a_0 as

$$a_0 = 5.292 \times 10^{-11} \text{ m} = 0.5292 \text{ \AA}$$

2. *How stable* the electron would be in that orbit—that is, its potential energy, E . This is given by

$$E = -\frac{1}{n^2} \left(\frac{h^2}{8\pi^2 m a_0^2} \right) = -\frac{2.180 \times 10^{-18} \text{ J}}{n^2}$$

where h = Planck's constant, m = the mass of the electron, and the other symbols have the same meaning as before. E is always negative when the electron is in the atom; $E = 0$ when the electron is completely removed from the atom ($n = \text{infinity}$).

Figure 4-19 shows the results of evaluating these equations for some of the possible values of n (1, 2, 3, ...). The larger the value of n , the farther from the nucleus is the orbit being described, and the radius of this orbit increases as the *square of n* increases. As n increases, n^2 increases, $1/n^2$ decreases, and thus the electronic energy increases (becomes less negative). For orbits farther from the nucleus, the electronic potential energy is higher (less negative—the electron is in a *higher* energy level or in a less stable state). Going away from the nucleus, the allowable orbits are farther apart in distance but closer together in energy. Consider the two possible limits of these equations. One limit is when $n = 1$; this describes the electron at the smallest possible distance from the nucleus and at its lowest (most negative) energy; the electron is at its most stable location. The other limit is for very large values of n , that is, as n approaches infinity. As this limit is approached, the electron is very far from the nucleus, or effectively removed from the atom; the potential energy is as high as possible, approaching zero; the electron is at its least stable location.

Each line in the emission spectrum represents the *difference in energies* between two allowed energy levels for the electron. When the electron goes from energy level n_2 to energy level n_1 , the difference in energy is given off as a single photon. The energy of this photon can be calculated from Bohr's equation for the energy, as follows.

$$E \text{ of photon} = E_2 - E_1 = \left(-\frac{2.180 \times 10^{-18} \text{ J}}{n_2^2} \right) - \left(-\frac{2.180 \times 10^{-18} \text{ J}}{n_1^2} \right)$$

Factoring out the constant $2.180 \times 10^{-18} \text{ J}$ and rearranging, we get

$$E \text{ of photon} = 2.180 \times 10^{-18} \text{ J} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

The Planck equation, $E = hc/\lambda$, relates the energy of the photon to the wavelength of the light, so

$$\frac{hc}{\lambda} = 2.180 \times 10^{-18} \text{ J} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Rearranging for $1/\lambda$, we obtain

$$\frac{1}{\lambda} = \frac{2.180 \times 10^{-18} \text{ J}}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

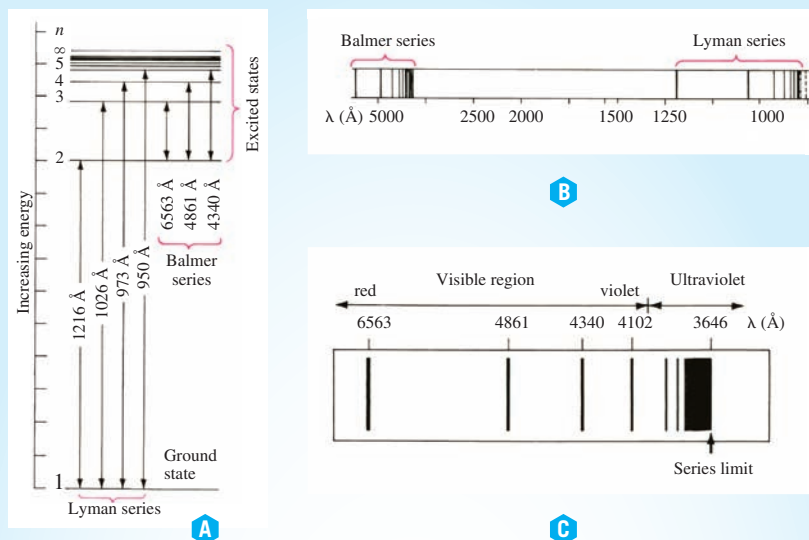


Figure 4-19 (a) The energy levels that the electron can occupy in a hydrogen atom and a few of the transitions that cause the emission spectrum of hydrogen. The numbers on the vertical lines show the wavelengths of light emitted when the electron falls to a lower energy level. (Light of the same wavelength is absorbed when the electron is excited to the higher energy level.) The difference in energy between two given levels is exactly the same for all hydrogen atoms, so it corresponds to a specific wavelength and to a specific line in the emission spectrum of hydrogen. In a given sample, some hydrogen atoms could have their electrons excited to the $n = 2$ level. These electrons could then fall to the $n = 1$ energy level, giving off the *difference* in energy in the form of light (the 1216-Å transition). Other hydrogen atoms might have their electrons excited to the $n = 3$ level; subsequently some could fall to the $n = 1$ level (the 1026-Å transition). Because higher energy levels become closer and closer in energy, *differences* in energy between successive transitions become smaller and smaller. The corresponding lines in the emission spectrum become closer together and eventually result in a continuum, a series of lines so close together that they are indistinguishable. (b) The emission spectrum of hydrogen. The series of lines produced by the electron falling to the $n = 1$ level is known as the *Lyman series*; it is in the ultraviolet region. A transition in which the electron falls to the $n = 2$ level gives rise to a similar set of lines in the visible region of the spectrum, known as the *Balmer series*. Other series involving transitions to energy levels with higher values of n are not shown. (c) The Balmer series shown on an expanded scale. The line at 6563 Å (the $n = 3 \rightarrow n = 2$ transition) is much more intense than the line at 4861 Å (the $n = 4 \rightarrow n = 2$ transition) because the first transition occurs much more frequently than the second. Successive lines in the spectrum become less intense as the series limit is approached because the transitions that correspond to these lines are less probable.

Comparing this to the Balmer–Rydberg equation, Bohr showed that the Rydberg constant is equivalent to $2.180 \times 10^{-18} \text{ J/hc}$. We can use the values for h and c to obtain the same value, $1.097 \times 10^7 \text{ m}^{-1}$, that was obtained by Rydberg on a solely empirical basis. Furthermore, Bohr showed the physical meaning of the two whole numbers n_1 and n_2 ; they represent the two energy states between which the transition takes place. Using this approach, Bohr was able to use fundamental constants to calculate the wavelengths of the observed lines in the hydrogen emission spectrum. Thus, Bohr’s application of the idea of quantization of energy to the electron in an atom provided the answer to a half-century-old puzzle concerning the discrete colors observed in emission and absorption spectra.



© Everett Collection Inc/Alamy

The Danish physicist Niels Bohr was one of the most influential scientists of the 20th century. Like many other now-famous physicists of his time, he worked for a time in England with J. J. Thomson and later with Ernest Rutherford. During this period, he began to develop the ideas that led to the publication of his explanation of atomic spectra and his theory of atomic structure, for which he received the Nobel Prize in Physics in 1922. After escaping from Nazi-occupied Denmark to Sweden in 1943, he helped to arrange the escape of hundreds of Danish Jews from the Hitler regime. He later went to the United States, where, until 1945, he worked with other scientists at Los Alamos, New Mexico, on the development of the atomic bomb. From then until his death in 1962, he worked for the development and use of atomic energy for peaceful purposes.



Various metals emit distinctive colors of visible light when heated to a high enough temperature (flame test). This is the basis for all fireworks, which use the salts of different metals such as strontium (red), barium (green), and copper (blue) to produce the beautiful colors.

We now accept the fact that electrons occupy only certain energy levels in atoms. In most atoms, some of the energy differences between levels correspond to the energy of visible light. Thus, colors associated with electronic transitions in such elements can be observed by the human eye.

Although the Bohr theory satisfactorily explained the spectra of hydrogen and of other species containing one electron (He^+ , Li^{2+} , etc.) the wavelengths in the observed spectra of more complex species could not be calculated. Bohr's assumption of circular orbits was modified in 1916 by Arnold Sommerfeld (1868–1951), who assumed elliptical orbits. Even so, the Bohr approach was doomed to failure, because it modified classical mechanics to solve a problem that could not be solved by classical mechanics. It was a contrived solution. This failure of classical mechanics set the stage for the development of a new physics, quantum mechanics, to deal with small particles. The Bohr theory, however, did introduce the ideas that only certain energy levels are possible, that these energy levels are described by quantum numbers that can have only certain allowed values, and that the quantum numbers indicate something about where and how stable the electrons are in these energy levels. The ideas of modern atomic theory have replaced Bohr's original theory. But his achievement in showing a link between electronic arrangements and Balmer and Rydberg's empirical description of light absorption, and in establishing the quantization of electronic energy, was a very important step toward an understanding of atomic structure.

Two big questions remained about electrons in atoms: (1) How are electrons arranged in atoms? (2) How do these electrons behave? We now have the background to describe how modern atomic theory answers these questions.

4-14 The Wave Nature of the Electron

► Be careful to distinguish between the letter v , which represents velocity, and the Greek letter ν , ν , which represents frequency (see Section 4-10).

Einstein's idea that light can exhibit both wave properties and particle properties suggested to Louis de Broglie (1892–1987) that very small particles, such as electrons, might also display wave properties under the proper circumstances. In his doctoral thesis in 1925, de Broglie predicted that a particle with a mass m and velocity v should have a wavelength associated with it. The numerical value of this de Broglie wavelength is given by

$$\lambda = h/mv \text{ (where } h = \text{Plank's constant)}$$

Two years after de Broglie's prediction, C. Davisson (1882–1958) and L. H. Germer (1896–1971) at the Bell Telephone Laboratories demonstrated diffraction of electrons by a crystal of nickel. This behavior is an important characteristic of waves. It shows conclusively that electrons do have wave properties. Davisson and Germer found that the wavelength associated with electrons of known energy is exactly that predicted by de Broglie. Similar diffraction experiments have been successfully performed with other particles, such as neutrons.

EXAMPLE 4-7 de Broglie Equation

- (a) Calculate the wavelength in meters of an electron traveling at 1.24×10^7 m/s. The mass of an electron is 9.11×10^{-28} g.
 (b) Calculate the wavelength of a baseball of mass 5.25 oz traveling at 92.5 mph. Recall that $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$.

Plan

For each calculation, we use the de Broglie equation

$$\lambda = \frac{h}{mv}$$



Materials scientists study electron diffraction patterns to learn about the surfaces of solids.

where

$$\begin{aligned} h \text{ (Planck's constant)} &= 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times \frac{1 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}}{1 \text{ J}} \\ &= 6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}} \end{aligned}$$

For consistency of units, mass must be expressed in kilograms. In part (b), we must also convert the speed to meters per second.

Solution

$$(a) \quad m = 9.11 \times 10^{-28} \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 9.11 \times 10^{-31} \text{ kg}$$

Substituting into the de Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}}}{(9.11 \times 10^{-31} \text{ kg}) \left(1.24 \times 10^7 \frac{\text{m}}{\text{s}} \right)} = 5.87 \times 10^{-11} \text{ m}$$

Though this seems like a very short wavelength, it is similar to the spacing between atoms in many crystals. A stream of such electrons hitting a crystal gives measurable diffraction patterns.

$$(b) \quad m = 5.25 \text{ oz} \times \frac{1 \text{ lb}}{16 \text{ oz}} \times \frac{1 \text{ kg}}{2.205 \text{ lb}} = 0.149 \text{ kg}$$

$$v = \frac{92.5 \text{ miles}}{\text{h}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{1.609 \text{ km}}{1 \text{ mile}} \times \frac{1000 \text{ m}}{1 \text{ km}} = 41.3 \frac{\text{m}}{\text{s}}$$

Now, we substitute into the de Broglie equation.

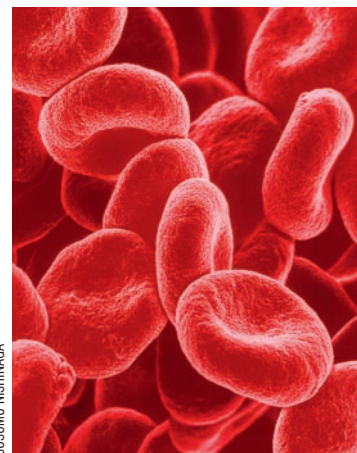
$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}}}{(0.149 \text{ kg}) \left(41.3 \frac{\text{m}}{\text{s}} \right)} = 1.08 \times 10^{-34} \text{ m}$$

This wavelength is far too short to give any measurable effects. Recall that atomic diameters are in the order of 10^{-10} m , which is 24 powers of 10 greater than the baseball “wavelength.”

You should now work Exercise 76.



A modern electron microscope.



A color-enhanced scanning electron micrograph of human red blood cells, magnified 1200X.

As you can see from the results of Example 4-7, the particles of the subatomic world behave very differently from the macroscopic objects with which we are familiar. To talk about the behavior of atoms and their particles, we must give up many of our long-held views about the behavior of matter. We must be willing to visualize a world of new and unfamiliar properties, such as the ability to act in some ways like a particle and in other ways like a wave.

The wave behavior of electrons is exploited in the electron microscope. This instrument allows magnification of objects far too small to be seen with an ordinary light microscope.

Unless otherwise noted, all content on this page is © Cengage Learning.

4-15 The Quantum Mechanical Picture of the Atom

Through the work of de Broglie, Davisson and Germer, and others, we now know that electrons in atoms can be treated as waves more effectively than as small compact particles traveling in circular or elliptical orbits. Large objects such as golf balls and moving automobiles obey the laws of classical mechanics (Isaac Newton's laws), but very small particles such as electrons, atoms, and molecules do not. A different kind of mechanics, called **quantum mechanics**, which is based on the *wave* properties of matter, describes the behavior of very small particles much better. Quantization of energy is a consequence of these properties.

One of the underlying principles of quantum mechanics is that we cannot determine precisely the paths that electrons follow as they move about atomic nuclei. The **Heisenberg Uncertainty Principle**, stated in 1927 by Werner Heisenberg (1901–1976), is a theoretical assertion that is consistent with all experimental observations.

It is impossible to determine accurately both the momentum and the position of an electron (or any other very small particle) simultaneously.

► This is like trying to locate the position of a moving automobile by driving another automobile into it.

Momentum is mass times velocity, mv . Because electrons are so small and move so rapidly, their motion is usually detected by electromagnetic radiation. Photons that interact with electrons have about the same energies as the electrons. Consequently, the interaction of a photon with an electron severely disturbs the motion of the electron. It is not possible to determine simultaneously both the position and the velocity of an electron, so we use a statistical approach to describe the *probability* of finding an electron within specified regions in space.

With these ideas in mind, we list some basic ideas of quantum mechanics.

1. Atoms and molecules can exist only in certain energy states. In each energy state, the atom or molecule has a definite energy. When an atom or molecule changes its energy state, it must emit or absorb just enough energy to bring it to the new energy state (the quantum condition).

Atoms and molecules possess various forms of energy. Let's focus our attention on their *electronic energies*.

2. When atoms or molecules emit or absorb radiation (light), they change their energies. The energy change in the atom or molecule is related to the frequency or wavelength of the light emitted or absorbed by the equations:

► Recall that $\lambda\nu = c$, so $\nu = c/\lambda$.

$$\Delta E = h\nu \quad \text{or} \quad \Delta E = hc/\lambda$$

This gives a relationship between the energy change, ΔE , and the wavelength, λ , of the radiation emitted or absorbed. *The energy lost (or gained) by an atom as it goes from higher to lower (or lower to higher) energy states is equal to the energy of the photon emitted (or absorbed) during the transition.*

3. The allowed energy states of atoms and molecules can be described by sets of numbers called *quantum numbers*.

The mathematical approach of quantum mechanics involves treating the electron in an atom as a *standing wave*. A standing wave is a wave that does not travel and therefore has at least one point at which it has zero amplitude, called a node. As an example, consider the various ways that a guitar string can vibrate when it is plucked (Figure 4-20). Because both ends are fixed (nodes), the string can vibrate only in ways in which there is a whole number of *half-wavelengths* in the length of the string (Figure 4-20a). Any possible motion of the string can be described as some combination of these allowed vibrations. In a similar way, we can imagine that the electron in the hydrogen atom behaves as a wave (recall the de Broglie relationship in the last section). The electron can be described by the same kind of standing-wave mathematics that is applied to a vibrating string. In this approach, the electron is characterized by a three-dimensional wave function, ψ . In a given space around the

nucleus, only certain “waves” can exist. Each “allowed wave” is called an **orbital** and corresponds to a stable energy state for the electron and is described by a particular set of quantum numbers.

The quantum mechanical treatment of atoms and molecules is highly mathematical. The important point is that each solution of the Schrödinger wave equation (see the following Enrichment section) describes a possible energy state for the electrons in the atom. Each solution is described by a set of **quantum numbers**. These numbers are in accord with those deduced from experiment and from empirical equations such as the Balmer–Rydberg equation. Solutions of the Schrödinger equation also tell us about the shapes and orientations of the probability distributions of the electrons. (The Heisenberg Principle implies that this is how we must describe the positions of the electrons.) These *atomic orbitals* (which are described in Section 4-17) are deduced from the solutions of the Schrödinger equation. The orbitals are defined by the quantum numbers.

ENRICHMENT

The Schrödinger Equation

In 1926 Erwin Schrödinger (1887–1961) modified an existing equation that described a three-dimensional standing wave by imposing wavelength restrictions suggested by de Broglie’s ideas. The modified equation allowed him to calculate the energy levels in the hydrogen atom. It is a differential equation that need not be memorized or even understood to read this book. A knowledge of differential calculus would be necessary to solve it.

$$-\frac{\hbar^2}{8\pi^2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi = E\psi$$

This equation has been solved exactly only for one-electron species such as the hydrogen atom and the ions He^+ and Li^{2+} . Simplifying assumptions are necessary to solve the equation for more complex atoms and molecules. Chemists and physicists have used their intuition and ingenuity (and modern computers), however, to apply this equation to more complex systems.

In 1928 Paul A. M. Dirac (1902–1984) reformulated electron quantum mechanics to take into account the effects of relativity. This gave rise to an additional quantum number.

4-16 Quantum Numbers

The solutions of the Schrödinger and Dirac equations for hydrogen atoms give wave functions, ψ , that describe the various states available to hydrogen’s single electron. Each of these possible states is described by four quantum numbers. We can use these quantum numbers to designate the electronic arrangements in all atoms, their so-called **electron configurations**. These quantum numbers play important roles in describing the energy levels of electrons and the shapes of the orbitals that describe distributions of electrons in space. The interpretation will become clearer when we discuss atomic orbitals in the following section. For now, let’s say that

an **atomic orbital** is a region of space in which the probability of finding an electron is high.

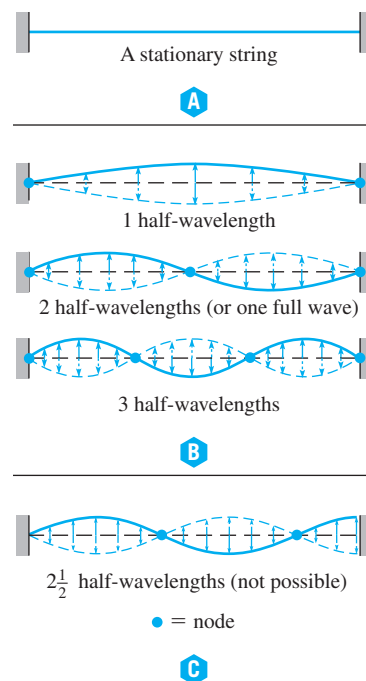


Figure 4-20 When a stationary string that is fixed at both ends, such as a guitar or piano string (a) is plucked or struck, it has a number of natural patterns of vibration, called normal modes. Because the string is fixed at both ends, the ends must be stationary. Each different possible vibration is a standing wave and can be described by a wave function. The only waves that are possible are those in which a whole number of half-wavelengths fits into the string length. These allowed waves constitute a harmonic series. Any total motion of the string is some combination of these allowed harmonics. (b) Some of the ways in which a plucked string can vibrate. The position of the string at one extreme of each vibration is shown as a solid line, and at the other extreme as a dashed line. (c) An example of vibration that is *not* possible for a plucked string. In such a vibration, an end of the string would move; this is not possible because the ends are fixed.

Let's define each quantum number and describe the range of values it may take.

1. The **principal quantum number**, n , describes the *main energy level*, or shell, that an electron occupies. It may be any positive integer:

$$n = 1, 2, 3, 4, \dots$$

2. Within a shell (defined by the value of n , the principal quantum number), different sublevels or subshells are possible, each with a characteristic shape. The **angular momentum quantum number**, ℓ , designates a *sublevel*, or a specific *shape* of atomic orbital that an electron may occupy. This number, ℓ , may take integral values from 0 up to and including $(n - 1)$:

$$\ell = 0, 1, 2, \dots, (n - 1)$$

Thus, the maximum value of ℓ is $(n - 1)$. We give a letter notation to each value of ℓ . Each letter corresponds to a different sublevel (subshell) and a differently shaped orbital:

$$\ell = 0, 1, 2, 3, \dots, (n - 1)$$

$s \quad p \quad d \quad f$

► The s, p, d, f designations arise from the characteristics of spectral emission lines produced by electrons occupying the orbitals: s (sharp), p (principal), d (diffuse), and f (fundamental).

In the first shell, the maximum value of ℓ is zero, which tells us that there is only an s subshell and no p subshell. In the second shell, the permissible values of ℓ are 0 and 1, which tells us that there are only s and p subshells.

3. Orbitals within a given subshell differ in their orientations in space, but not in their energies. The **magnetic quantum number**, m_ℓ , designates a specific orbital within a subshell. Within each subshell, m_ℓ may take any integral values from $-\ell$ through zero up to and including $+\ell$:

$$m_\ell = (-\ell), \dots, 0, \dots, (+\ell)$$

The maximum value of m_ℓ depends on the value of ℓ . For example, when $\ell = 1$, which designates the p subshell, there are three permissible values of m_ℓ : -1 , 0 , and $+1$. Thus, three distinct regions of space, called atomic orbitals, are associated with a p subshell. We refer to these orbitals as the p_x , p_y , and p_z orbitals (see Section 4-17).

4. The **spin quantum number**, m_s , refers to the spin of an electron and the orientation of the magnetic field produced by this spin. For every set of n , ℓ , and m_ℓ values, m_s can take the value $+\frac{1}{2}$ or $-\frac{1}{2}$:

$$m_s = \pm \frac{1}{2}$$

The values of n , ℓ , and m_ℓ describe a particular atomic orbital. Each atomic orbital can accommodate no more than two electrons, one with $m_s = +\frac{1}{2}$ and another with $m_s = -\frac{1}{2}$.

Table 4-8 summarizes some permissible values for the four quantum numbers. Spectroscopic evidence confirms the quantum mechanical predictions about the number of atomic orbitals in each shell.

4-17 Atomic Orbitals

Let's now describe the distributions of electrons in atoms. For each neutral atom, we must account for a number of electrons equal to the number of protons in the nucleus, that is, the atomic number of the atom. Each electron is said to occupy an atomic orbital defined by a set of quantum numbers n , ℓ , and m_ℓ . In any atom, each orbital can hold a maximum of two electrons (m_s values of $+\frac{1}{2}$ and $-\frac{1}{2}$). Within each atom, these atomic orbitals, taken together, can be represented as a diffuse cloud of electrons (Figure 4-21).

The main shell of each atomic orbital in an atom is indicated by the principal quantum number n (from the Schrödinger equation). As we have seen, the principal quantum number takes integral values: $n = 1, 2, 3, 4, \dots$. The value $n = 1$ describes the first, or innermost, shell. These shells have been referred to as electron energy levels. Successive shells

► The subscripts x , y , and z refer to the axes on a Cartesian coordinate system. The p_x orbital, for example, lies along the positive and negative directions of the x axis with the nucleus located at the origin (see Figure 4-25).

Table 4-8 Permissible Values of the Quantum Numbers Through $n = 4$

n	ℓ	m_ℓ	m_s	Electron Capacity of Subshell = $4\ell + 2$	Electron Capacity of Shell = $2n^2$
1	0(1s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	2
2	0(2s) 1(2p)	0 -1, 0, +1	$+\frac{1}{2}, -\frac{1}{2}$ $\pm\frac{1}{2}$ for each value of m_ℓ	2 6	8
3	0(3s) 1(3p) 2(3d)	0 -1, 0, +1 -2, -1, 0, +1, +2	$+\frac{1}{2}, -\frac{1}{2}$ $\pm\frac{1}{2}$ for each value of m_ℓ $\pm\frac{1}{2}$ for each value of m_ℓ	2 6 10	18
4	0(4s) 1(4p) 2(4d) 3(4f)	0 -1, 0, +1 -2, -1, 0, +1, +2 -3, -2, -1, 0, +1, +2, +3	$+\frac{1}{2}, -\frac{1}{2}$ $\pm\frac{1}{2}$ for each value of m_ℓ $\pm\frac{1}{2}$ for each value of m_ℓ $\pm\frac{1}{2}$ for each value of m_ℓ	2 6 10 14	32

are at increasingly greater distances from the nucleus. For example, the $n = 2$ shell is farther from the nucleus than the $n = 1$ shell. The electron capacity of each shell is indicated in the right-hand column of Table 4-8. For a given n , the capacity is $2n^2$.

By the rules given in Section 4-16, each shell has an s subshell (defined by $\ell = 0$) consisting of one s atomic orbital (defined by $m_\ell = 0$). We distinguish among orbitals in different principal shells (main energy levels) by using the principal quantum number as a coefficient; $1s$ indicates the s orbital in the first shell, $2s$ is the s orbital in the second shell, $2p$ is a p orbital in the second shell, and so on (see Table 4-8).

For each solution to the quantum mechanical equation, we can calculate the electron probability density (sometimes just called the electron density) at each point in the atom. This is the probability of finding an electron at that point. It can be shown that this electron density is proportional to $r^2\psi^2$, where r is the distance from the nucleus.

In the graphs in Figure 4-22, the electron probability density at a given distance from the nucleus is plotted against distance from the nucleus, for s orbitals. It is found that the electron probability density curve is the same regardless of the direction in the atom. We describe an s orbital as *spherically symmetrical*; that is, it is round like a basketball (Figure 4-23). The electron clouds (electron densities) associated with the $1s$, $2s$, and $3s$ atomic orbitals are shown just below the plots in Figure 4-22. The electron clouds are three-dimensional, and only cross sections are shown here. The regions shown in some figures (Figures 4-23 through 4-27) appear to have surfaces or skins only because they are arbitrarily “cut off” so that there is a 90% probability of finding an electron occupying the orbital somewhere within the volume defined by the surface.

► As you study the next two sections, keep in mind that the wave function, ψ , for an orbital characterizes two features of an electron in that orbital: (1) *where* (the region in space) the probability of finding the electron is high and (2) *how stable* that electron is (its energy).

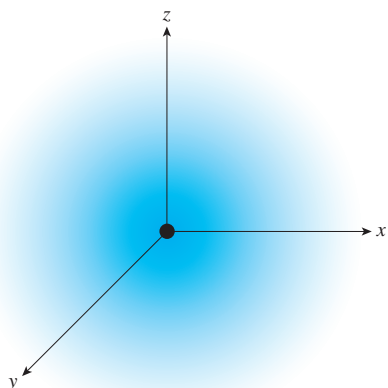


Figure 4-21 An electron cloud surrounding an atomic nucleus. The electron density drops off rapidly but smoothly as distance from the nucleus increases.

Unless otherwise noted, all content on this page is © Cengage Learning.

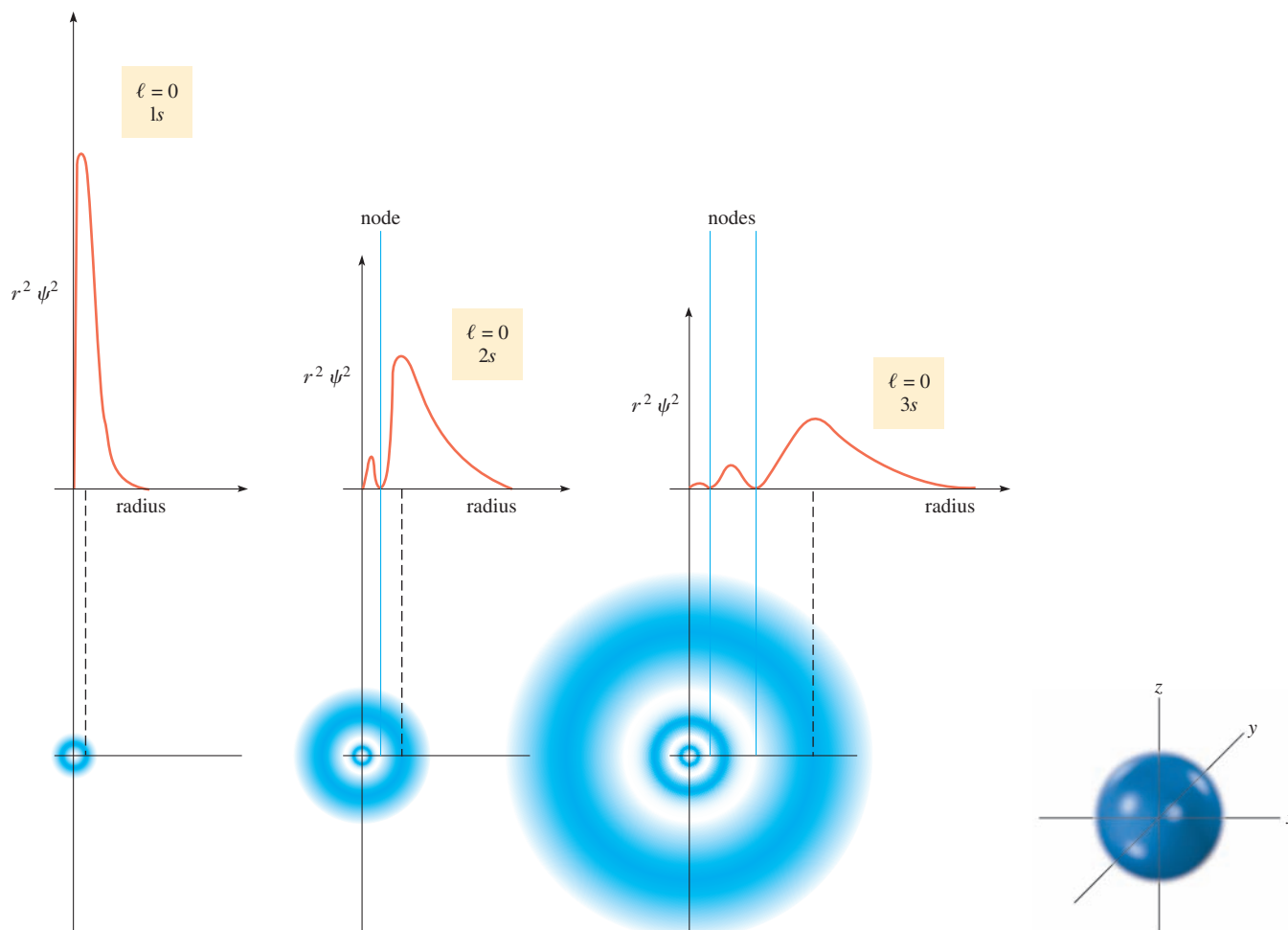


Figure 4-22 Plots of the electron density distributions associated with s orbitals. For any s orbital, this plot is the same in any direction (orbital is spherically symmetrical). The sketch below each plot shows a cross section, in the plane of the atomic nucleus, of the electron cloud associated with that orbital. Electron density is proportional to $r^2 \psi^2$. s orbitals with $n > 1$ have $n - 1$ regions where the electron density drops to zero. These are indicated by blue vertical lines on the plots, indicating where the electron density drops to zero (nodes), and by the white regions on the cross section.

Figure 4-23 The shape of an s orbital.

Beginning with the second shell, each shell also contains a p subshell, defined by $\ell = 1$. Each of these subshells consists of a set of *three* p atomic orbitals, corresponding to the three allowed values of m_ℓ (-1 , 0 , and $+1$) when $\ell = 1$. The sets are referred to as $2p$, $3p$, $4p$, $5p$, ... orbitals to indicate the main shells in which they are found. Each set of atomic p orbitals resembles three mutually perpendicular equal-arm flattened dumbbells (see Figure 4-24). Each p orbital has a nodal plane (blue lines/planes in Figure 4-24) in which there is zero probability of finding the electron. The two regions in which the electron probability is nonzero are on opposite sides of this nodal plane and are referred to as the *lobes* of the p orbital. Each electron in a p orbital has equal probability of being in either lobe. In the two lobes, the wave ψ represents that the electron has opposite *phases*, corresponding to the crests and troughs of water waves in Figure 4-12. These phases correspond to mathematical wave functions with positive and negative signs, but these signs *do not* represent charges. The nucleus defines the origin of a set of Cartesian coordinates with the usual x , y , and z axes (see Figure 4-25a). The subscript x , y , or z indicates the axis along which each of the orbitals is directed. A set of three p atomic orbitals may be represented as in Figure 4-25b.

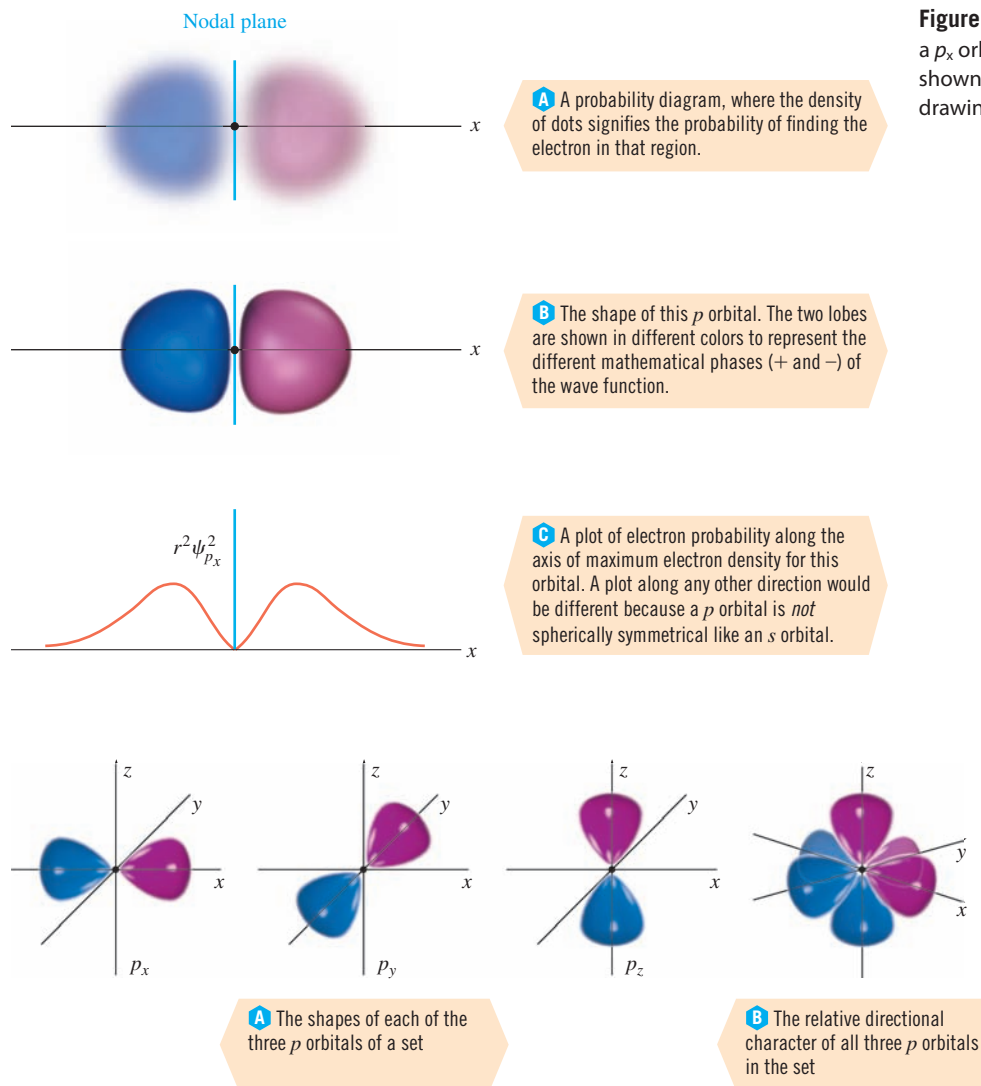


Figure 4-25 Representation of p orbitals.

Beginning at the third shell, each shell also contains a third subshell ($\ell = 2$) composed of a set of *five* d atomic orbitals ($m_\ell = -2, -1, 0, +1, +2$). They are designated $3d$, $4d$, $5d$, ... to indicate the shell in which they are found. The shapes of the members of a set are indicated in Figure 4-26.

► Some excellent visual representations of orbital shapes can be seen at www.winter.group.shef.ac.uk/orbitron

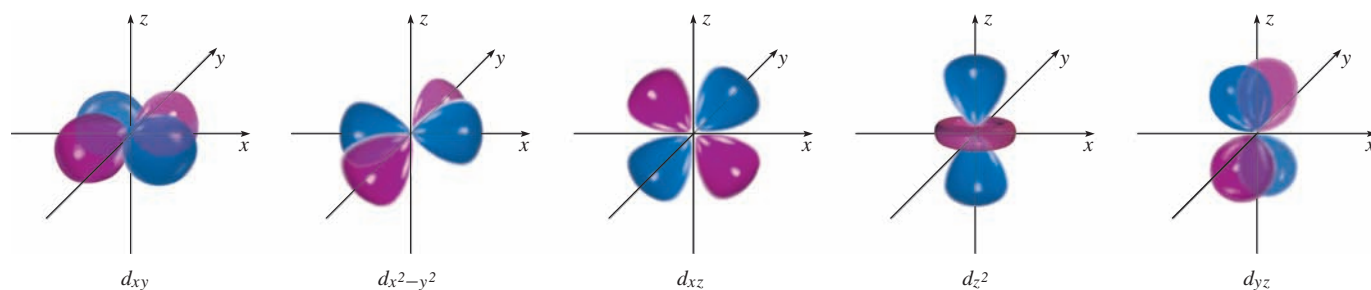


Figure 4-26 Spatial orientation of d orbitals. Note that the lobes of the $d_{x^2-y^2}$ and d_{z^2} orbitals lie along the axes, whereas the lobes of the others lie along diagonals between the axes.

Unless otherwise noted, all content on this page is © Cengage Learning.

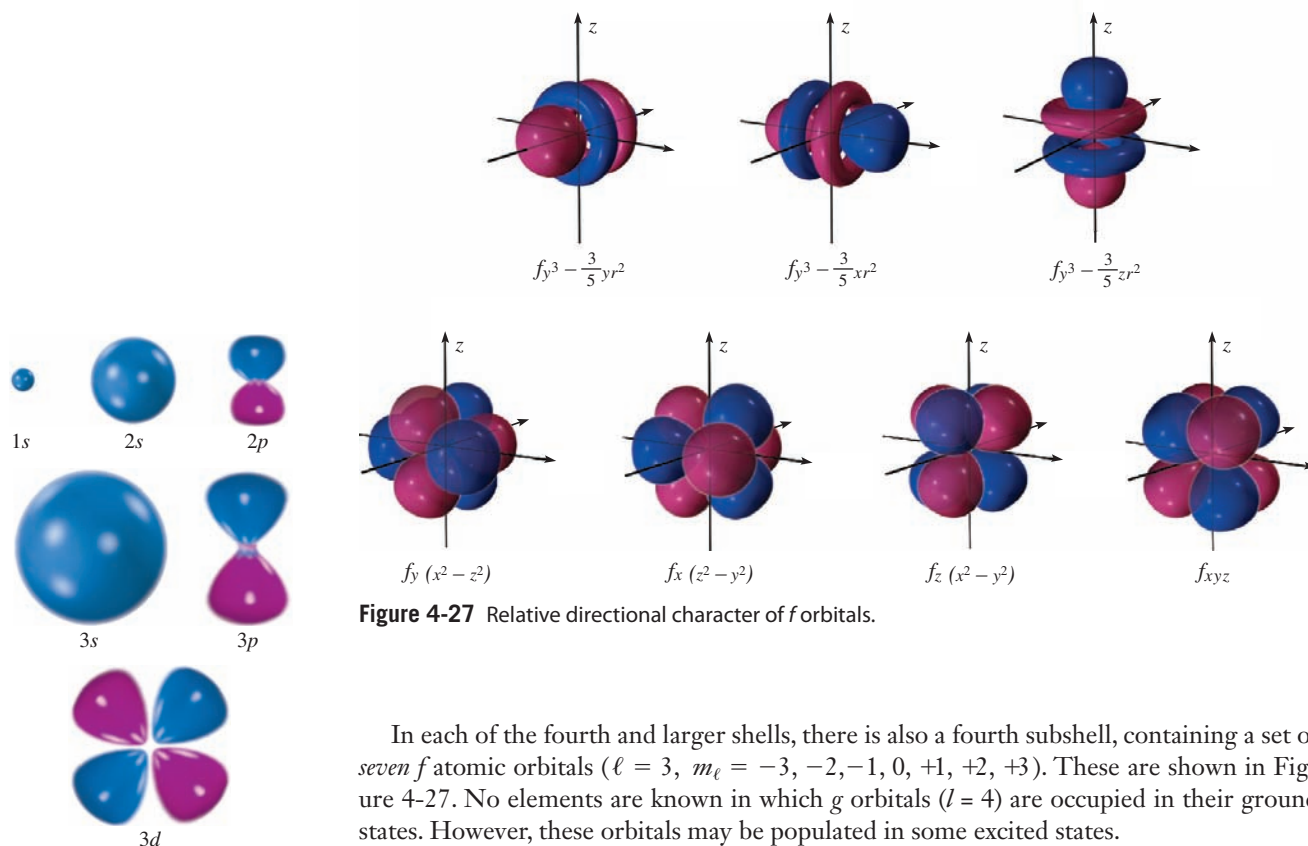


Figure 4-27 Relative directional character of f orbitals.

Figure 4-28 Shapes and approximate relative sizes of several orbitals in an atom.

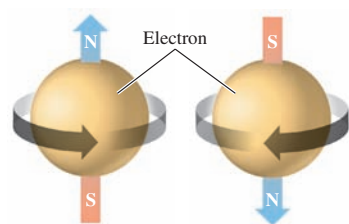


Figure 4-29 Electron spin. Electrons act as though they spin about an axis through their centers. Electrons may spin in either of two directions, so the spin quantum number has two possible values, $+\frac{1}{2}$ and $-\frac{1}{2}$, sometimes referred to as “spin up” or “spin down.” Each electron spin produces a magnetic field. When two electrons have opposite spins (gray arrows), the attraction due to their opposite magnetic fields (red/blue arrows) helps to overcome the repulsion of their like charges. This permits two electrons to occupy the same region (orbital).

In each of the fourth and larger shells, there is also a fourth subshell, containing a set of seven f atomic orbitals ($\ell = 3$, $m_\ell = -3, -2, -1, 0, +1, +2, +3$). These are shown in Figure 4-27. No elements are known in which g orbitals ($\ell = 4$) are occupied in their ground states. However, these orbitals may be populated in some excited states.

Thus, we see the first shell contains only the $1s$ orbital; the second shell contains the $2s$ and three $2p$ orbitals; the third shell contains the $3s$, three $3p$, and five $3d$ orbitals; and the fourth shell consists of a $4s$, three $4p$, five $4d$, and seven $4f$ orbitals. All subsequent shells contain s , p , d , and f subshells as well as others that are not occupied in any presently known elements in their lowest energy states.

The sizes of orbitals increase with increasing n , as shown in Figure 4-28. How do we know the sizes of orbitals and the relationship between the value of n and orbital size? Experiments such as density measurements provide information about atomic radii, and thus about the sizes of the outermost orbitals. In addition, calculations and models of the orbitals enable us to make correct predictions. Figure 4-28 shows an example of the relationship between n and the size of the orbitals. We will find the following generalizations about orbital sizes useful:

1. In any atom, all orbitals with the same principal quantum number n are similar in size.
2. In an atom, larger values of n correspond to larger orbital size.
3. Each orbital with a given n value becomes smaller as nuclear charge increases.

The directions of p , d , and f orbitals, however, are easier to visualize in drawings such as those shown for p orbitals in Figure 4-25b; therefore, most chemists use such “slenderized” representations.

In this section, we haven’t yet discussed the fourth quantum number, the spin quantum number, m_s . Because m_s has two possible values, $+\frac{1}{2}$ and $-\frac{1}{2}$, each atomic orbital, defined by the values of n , ℓ , and m_ℓ , has a capacity of two electrons. Electrons are negatively charged, and they behave as though they were spinning about axes through their centers, so they act like tiny magnets. The motions of electrons produce magnetic fields, and these can interact with one another. Two electrons in the same orbital having opposite m_s values are said to be **spin-paired**, or simply **paired** (Figure 4-29).

Let’s summarize, in tabular form, some of the information we have developed to this point. The principal quantum number n indicates the main shell. The number of subshells per shell is equal to n , the number of atomic orbitals per shell is n^2 , and the maxi-

maximum number of electrons per shell is $2n^2$, because each atomic orbital can hold two electrons.

Shell n	Number of Subshells per Shell n	Number of Atomic Orbitals n^2	Maximum Number of Electrons $2n^2$
1	1	1 ($1s$)	2
2	2	4 ($2s, 2p_x, 2p_y, 2p_z$)	8
3	3	9 ($3s$, three $3p$'s, five $3d$'s)	18
4	4	16	32
5	5	25	50

4-18 Electron Configurations

The wave function for an atom simultaneously depends on (describes) all the electrons in the atom. The Schrödinger equation is much more complicated for atoms with more than one electron than for a one-electron species such as a hydrogen atom, and an explicit solution to this equation is not possible even for helium, let alone for more complicated atoms. We must therefore rely on approximations to solutions of the many-electron Schrödinger equation. One of the most common and useful of these is the *orbital approximation*. In this approximation, the electron cloud of an atom is assumed to be the superposition of charge clouds, or orbitals, arising from the individual electrons; these orbitals resemble the atomic orbitals of hydrogen (for which exact solutions are known), which we described in some detail in the previous section. Each electron is described by the same allowed combinations of quantum numbers (n , ℓ , m_ℓ , and m_s) that we used for the hydrogen atom; however, the order of energies of the orbitals is often different from that in hydrogen.

Let us now examine the electronic structures of atoms of different elements. The electronic arrangement that we will describe for each atom is called the **ground state** electron configuration. This corresponds to the isolated atom in its lowest energy, or unexcited, state. Electron configurations for the elements, as verified by experiment, are given in Appendix B. We will consider the elements in order of increasing atomic number, using the periodic table as our guide.

In describing a ground state electron configuration, the guiding idea is that the *total energy* of the atom is as low as possible. To determine these configurations, we use the **Aufbau Principle** as a guide:

Each atom is “built up” by (1) adding the appropriate numbers of protons and neutrons in the nucleus as specified by the atomic number and the mass number, and (2) adding the necessary number of electrons into orbitals in the way that gives the lowest *total energy* for the atom.

As we apply this principle, we will focus on the difference in electronic arrangement between a given element and the element with an atomic number that is one lower. In doing this, we emphasize the particular electron that distinguishes each element from the previous one; however, we should remember that this distinction is artificial because electrons are not really distinguishable. Though we do not always point it out, we *must* keep in mind that the atomic number (the charge on the nucleus) also differs from one element to the next.

The orbitals increase in energy with increasing value of the quantum number n . For a given value of n , energy increases with increasing value of ℓ . In other words, within a particular main shell, the s subshell is lowest in energy, the p subshell is the next lowest, then the d , then the f , and so on. As a result of changes in the nuclear charge and interactions among the electrons in the atom, the order of energies of the orbitals can vary somewhat from atom to atom.

► The great power of modern computers has allowed scientists to make numerical approximations to this solution to very high accuracy for simple atoms such as helium. As the number of electrons increases, however, even such numerical approaches become more difficult to apply and interpret. For multielectron atoms, more qualitative approximations are used.

► The German verb *aufbauen* means “to build up.”

Two general rules help us to predict electron configurations.

1. Electrons are assigned to orbitals in order of increasing value of $(n + \ell)$.
2. For subshells with the same value of $(n + \ell)$, electrons are assigned first to the subshell with lower n .

For example, the $2s$ subshell has $(n + \ell = 2 + 0 = 2)$, and the $2p$ subshell has $(n + \ell = 2 + 1 = 3)$, so we would expect to fill the $2s$ subshell before the $2p$ subshell (Rule 1). This rule also predicts that the $4s$ subshell $(n + \ell = 4 + 0 = 4)$ will fill before the $3d$ subshell $(n + \ell = 3 + 2 = 5)$. Rule 2 reminds us to fill $2p$ $(n + \ell = 2 + 1 = 3)$ before $3s$ $(n + \ell = 3 + 0 = 3)$ because $2p$ has a lower value of n . The *usual* order of energies of orbitals of an atom and a helpful reminder of this order are shown in Figures 4-30 and 4-31.

But we should consider these rules as just a *guide* to predicting electron arrangements. The observed electron configurations of lowest total energy do not always match those predicted by the Aufbau guide, and we will see a number of exceptions, especially for elements in the B groups (transition metals) of the periodic table.

The electronic structures of atoms are governed by the **Pauli Exclusion Principle**:

No two electrons in an atom may have identical sets of four quantum numbers.

An orbital is described by a particular allowed set of values for n , ℓ , and m_ℓ . Two electrons can occupy the same orbital only if they have opposite spins, m_s (see Figure 4-29). Two such electrons in the same orbital are said to be *spin-paired*, or simply *paired*. A single electron that occupies an orbital by itself is said to be *unpaired*. For simplicity, we shall indicate atomic orbitals as $\underline{\hspace{0.5cm}}$ and show an unpaired electron as $\uparrow$ and paired electrons as $\uparrow\downarrow$.

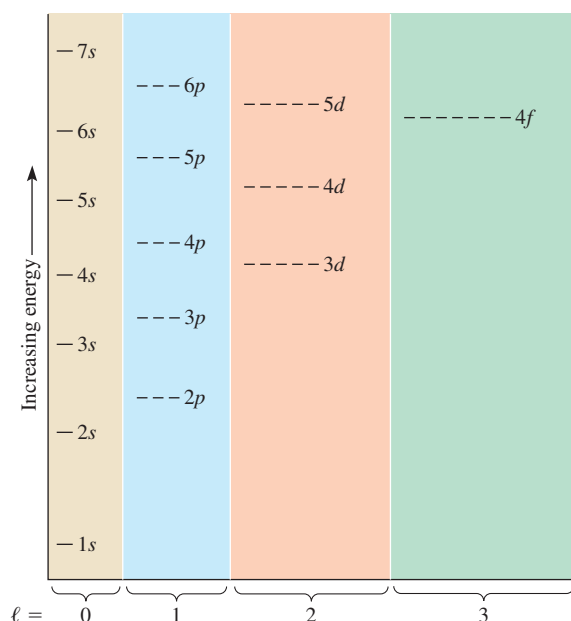


Figure 4-30 The usual order of filling (Aufbau order) of the orbitals of an atom, based on the two rules presented above. The relative energies are different for different elements, but the following main features should be noted: (1) The largest energy gap is between the $1s$ and $2s$ orbitals. (2) The energies of orbitals are generally closer together at higher energies. (3) The gap between np and $(n + 1)s$ (e.g., between $2p$ and $3s$ or between $3p$ and $4s$) is fairly large. (4) The gap between $(n - 1)d$ and ns (e.g., between $3d$ and $4s$) is quite small. (5) The gap between $(n - 2)f$ and ns (e.g., between $4f$ and $6s$) is even smaller.

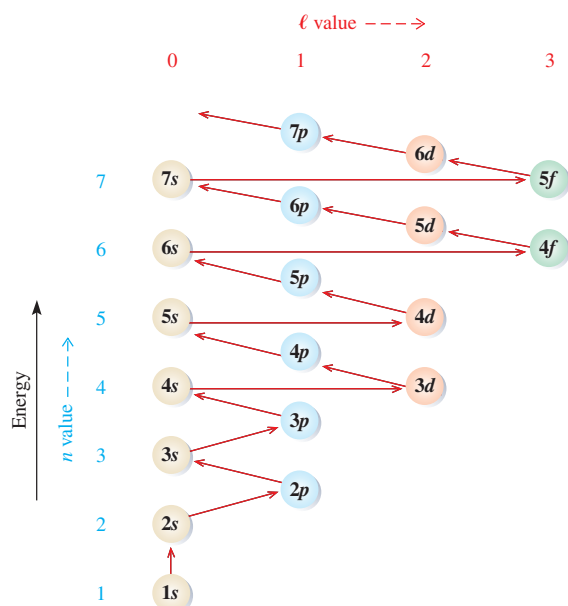


Figure 4-31 An aid to remembering the usual order of filling (Aufbau order) of atomic orbitals.

Row 1. The first shell consists of only one atomic orbital, $1s$. This can hold a maximum of two electrons. Hydrogen, as we have already noted, contains just one electron. Helium, a noble gas, has a filled first main shell (two electrons) and is so stable that no chemical reactions of helium are known.

	Orbital Notation		Simplified Notation
	$1s$		
${}_1\text{H}$	$\uparrow$		$1s^1$
${}_2\text{He}$	$\uparrow\downarrow$		$1s^2$

principal quantum number n

$1s^2$

number of electrons in orbital or set of equivalent orbitals

angular momentum quantum number ℓ

In the simplified notation, we indicate with superscripts the number of electrons in each subshell.

Row 2. Elements of atomic numbers 3 through 10 occupy the second period, or horizontal row, in the periodic table. In neon atoms the second main shell is filled completely. Neon, a noble gas, is extremely stable. No reactions of it are known.

	Orbital Notation			Simplified Notation
	$1s$	$2s$	$2p$	
Li	$\uparrow\downarrow$	$\uparrow$		$1s^2 2s^1$ or $[\text{He}] 2s^1$
Be	$\uparrow\downarrow$	$\uparrow\downarrow$		$1s^2 2s^2$ or $[\text{He}] 2s^2$
B	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ — —	$1s^2 2s^2 2p^1$ or $[\text{He}] 2s^2 2p^1$
C	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ —	$1s^2 2s^2 2p^2$ or $[\text{He}] 2s^2 2p^2$
N	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ $\uparrow$	$1s^2 2s^2 2p^3$ or $[\text{He}] 2s^2 2p^3$
O	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow$ $\uparrow$	$1s^2 2s^2 2p^4$ or $[\text{He}] 2s^2 2p^4$
F	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$	$1s^2 2s^2 2p^5$ or $[\text{He}] 2s^2 2p^5$
Ne	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$1s^2 2s^2 2p^6$ or $[\text{He}] 2s^2 2p^6$

► In writing electron configurations of atoms, we frequently simplify the notations. The abbreviation $[\text{He}]$ indicates that the $1s$ orbital is completely filled, $1s^2$, as in helium.

We see that some atoms have unpaired electrons in the same set of energetically equivalent, or **degenerate**, orbitals. We have already seen that two electrons can occupy a given atomic orbital (with the same values of n , ℓ , and m_ℓ) *only* if their spins are paired (have opposite values of m_s). Even with pairing of spins, however, two electrons that are in the same orbital repel each other more strongly than do two electrons in different (but equal-energy) orbitals. Thus, both theory and experimental observations (see Section 4-18) lead to **Hund's Rule**:

Electrons occupy all the orbitals of a given subshell singly before pairing begins. These unpaired electrons have parallel spins.

Thus, carbon has two unpaired electrons in its $2p$ orbitals, and nitrogen has three.

Row 3. The next element beyond neon is sodium. Here we begin to add electrons to the third shell. Elements 11 through 18 occupy the third period in the periodic table.

	Orbital Notation		Simplified Notation
	3s	3p	
Na	[Ne] $\uparrow$		[Ne] $3s^1$
Mg	[Ne] $\uparrow\downarrow$		[Ne] $3s^2$
Al	[Ne] $\uparrow\downarrow$	$\uparrow$ — —	[Ne] $3s^2 3p^1$
Si	[Ne] $\uparrow\downarrow$	$\uparrow$ $\uparrow$ —	[Ne] $3s^2 3p^2$
P	[Ne] $\uparrow\downarrow$	$\uparrow$ $\uparrow$ $\uparrow$	[Ne] $3s^2 3p^3$
S	[Ne] $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow$ $\uparrow$	[Ne] $3s^2 3p^4$
Cl	[Ne] $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$	[Ne] $3s^2 3p^5$
Ar	[Ne] $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	[Ne] $3s^2 3p^6$

Although the third shell is not yet filled (the d orbitals are still empty), argon is a noble gas. All noble gases except helium have $ns^2 np^6$ electron configurations (where n indicates the largest occupied shell). The noble gases are quite unreactive.

Rows 4 and 5. It is observed experimentally that *each electron occupies the available orbital that gives the atom the lowest total energy*. It is observed that filling the $4s$ orbitals before electrons enter the $3d$ orbitals *usually* leads to a lower total energy for the atom than some other arrangements. We therefore fill the orbitals in this order (see Figure 4-30). According to the Aufbau order (recall Figures 4-30 and 4-31), $4s$ fills before $3d$. In general, *the $(n + 1)s$ orbital fills before the nd orbital*. This is sometimes referred to as the $(n + 1)s$ rule.

After the $3d$ sublevel is filled to its capacity of 10 electrons, the $4p$ orbitals fill next, taking us to the noble gas krypton. Then the $5s$ orbital, the five $4d$ orbitals, and the three $5p$ orbitals fill to take us to xenon, a noble gas.

Let's now examine the electronic structure of the 18 elements in the fourth period in some detail. Some of these have electrons in d orbitals.

	Orbital Notation			Simplified Notation
	3d	4s	4p	
K	[Ar]	$\uparrow$		[Ar] $4s^1$
Ca	[Ar]	$\uparrow\downarrow$		[Ar] $4s^2$
Sc	[Ar] $\uparrow$ — — —	$\uparrow\downarrow$		[Ar] $3d^1 4s^2$
Ti	[Ar] $\uparrow$ $\uparrow$ — —	$\uparrow\downarrow$		[Ar] $3d^2 4s^2$
V	[Ar] $\uparrow$ $\uparrow$ $\uparrow$ —	$\uparrow\downarrow$		[Ar] $3d^3 4s^2$
Cr	[Ar] $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$	$\uparrow$		[Ar] $3d^5 4s^1$
Mn	[Ar] $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$	$\uparrow\downarrow$		[Ar] $3d^5 4s^2$
Fe	[Ar] $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$	$\uparrow\downarrow$		[Ar] $3d^6 4s^2$
Co	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$ $\uparrow$	$\uparrow\downarrow$		[Ar] $3d^7 4s^2$
Ni	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$ $\uparrow$	$\uparrow\downarrow$		[Ar] $3d^8 4s^2$
Cu	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow$		[Ar] $3d^{10} 4s^1$
Zn	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$		[Ar] $3d^{10} 4s^2$
Ga	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ — —	[Ar] $3d^{10} 4s^2 4p^1$
Ge	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ —	[Ar] $3d^{10} 4s^2 4p^2$
As	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$ $\uparrow$ $\uparrow$	[Ar] $3d^{10} 4s^2 4p^3$
Se	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow$ $\uparrow$	[Ar] $3d^{10} 4s^2 4p^4$
Br	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$	[Ar] $3d^{10} 4s^2 4p^5$
Kr	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	[Ar] $3d^{10} 4s^2 4p^6$

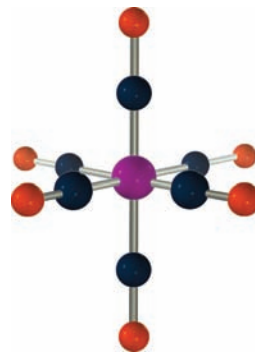
As you study these electron configurations, you should be able to see how most of them are predicted from the Aufbau order. However, as we fill the $3d$ set of orbitals, from Sc to Zn, we see that these orbitals are not filled quite regularly. As the $3d$ orbitals are filled, their energies get closer to that of the $4s$ orbital and eventually become lower. If the order of filling of electrons on chromium gave the expected configuration, it would be: $[\text{Ar}] 4s^2 3d^4$. Chemical and spectroscopic evidence indicates, however, that the configuration of Cr has only one electron in the $4s$ orbital, $[\text{Ar}] 4s^1 3d^5$. For this element, the $4s$ and $3d$ orbitals are nearly equal in energy. Six electrons in these six orbitals of nearly the same energy are more stable with the electrons all unpaired, $[\text{Ar}] 3d \uparrow \uparrow \uparrow \uparrow \uparrow 4s \uparrow$ rather than the predicted order $[\text{Ar}] 3d \uparrow \uparrow \uparrow \uparrow \uparrow 4s \uparrow \downarrow$.

The next elements, Mn to Ni, have configurations as predicted by the Aufbau order, presumably because forming a pair of electrons in the larger $4s$ orbital is easier than in a smaller, less diffuse $3d$ orbital. By the time Cu is reached, the energy of $3d$ is sufficiently lower than that of $4s$ so that the total energy of the configuration $[\text{Ar}] 4s^1 3d^{10}$ is lower than that of $[\text{Ar}] 4s^2 3d^9$.

We notice that the exceptions for Cr and Cu give half-filled or filled sets of equivalent orbitals (d^5 and d^{10} , respectively), and this is also true for several other exceptions to the Aufbau order. You may wonder why such an exception does not occur in, for example, Si or Ge, where we could have an $s^1 p^3$ configuration that would have half-filled sets of s and p orbitals. It does not occur because of the very large energy gap between ns and np orbitals. There is some evidence that does, however, suggest an enhanced stability of half-filled sets of p orbitals.

The electron configurations for the transition metals discussed here and in Appendix B are for individual metal atoms in the gas phase. Most chemists work with the transition metals either in the metallic state or as coordination compounds (see Chapter 25). A solid transition metal has a band structure of overlapping d and s orbital levels (see Section 13-7). When transition metal atoms have other types of atoms or molecules bonded to them, however, the electronic configuration usually becomes simpler in that the d orbitals fill first, followed by the next higher s orbital. This is illustrated by Cr, which has a $4s^1 3d^5$ electronic configuration as a free atom in the gas phase. But in the compound $\text{Cr}(\text{CO})_6$, chromium hexacarbonyl, which contains a central Cr atom surrounded by six neutral carbon monoxide (or carbonyl) groups, the chromium atom has a $3d^6$ electronic configuration.

► End-of-chapter Exercises 95–129 provide much valuable practice in writing electron configurations.



Ball-and-stick model of $\text{Cr}(\text{CO})_6$ (Cr = purple, C = black, O = red)

Problem-Solving Tip Exceptions to the Aufbau Order

In Appendix B, you will find a number of exceptions to the electron configurations predicted from the Aufbau Principle. You should realize that statements such as the Aufbau Principle and the $(n + 1)$ rule merely represent general guidelines and should not be viewed as hard-and-fast rules; exceptions occur to make the *total energy* of the atom as low as possible. Some of the reasons for exceptions are

1. The Aufbau order of orbital energies is based on calculations for the hydrogen atom, which contains only one electron. The orbital energies also depend on additional factors such as the nuclear charge and interactions of electrons in different occupied orbitals.
2. The energy scale varies with the atomic number.
3. Some orbitals are very close together, so their order can change, depending on the occupancies of other orbitals.

Some types of exceptions to the Aufbau order are general enough to remember easily, for example, those based on the special stability of filled or half-filled sets of orbitals. Other exceptions are quite unpredictable. Your instructor may expect you to remember some of the exceptions.

Let us now write the quantum numbers to describe each electron in an atom of nitrogen. Keep in mind the fact that Hund's Rule must be obeyed. Thus, there is only one (unpaired) electron in each $2p$ orbital in a nitrogen atom.

EXAMPLE 4-8 Electron Configurations and Quantum Numbers

Write an acceptable set of four quantum numbers for each electron in a nitrogen atom.

Plan

Nitrogen has seven electrons, which occupy the lowest energy orbitals available. Two electrons can occupy the first shell, $n = 1$, in which there is only one s orbital; when $n = 1$, then, ℓ must be zero, and therefore $m_\ell = 0$. The two electrons differ only in spin quantum number, m_s . The next five electrons can all fit into the second shell, for which $n = 2$ and ℓ may be either 0 or 1. The $\ell = 0$ (s) subshell fills first, and the $\ell = 1$ (p) subshell is occupied next.

Solution

► Electrons are indistinguishable. We have numbered them 1, 2, 3, and so on as an aid to counting them.

► In the lowest energy configurations, the three $2p$ electrons either have $m_s = +\frac{1}{2}$ or all have $m_s = -\frac{1}{2}$.

Electron	n	ℓ	m_ℓ	m_s	e^- Configuration
1, 2	$\left\{ \begin{array}{c} 1 \\ 1 \end{array} \right\}$	$\left\{ \begin{array}{c} 0 \\ 0 \end{array} \right\}$	$\left\{ \begin{array}{c} 0 \\ 0 \end{array} \right\}$	$\left\{ \begin{array}{c} +\frac{1}{2} \\ -\frac{1}{2} \end{array} \right\}$	$1s^2$
3, 4	$\left\{ \begin{array}{c} 2 \\ 2 \end{array} \right\}$	$\left\{ \begin{array}{c} 0 \\ 0 \end{array} \right\}$	$\left\{ \begin{array}{c} 0 \\ 0 \end{array} \right\}$	$\left\{ \begin{array}{c} +\frac{1}{2} \\ -\frac{1}{2} \end{array} \right\}$	$2s^2$
5, 6, 7	$\left\{ \begin{array}{c} 2 \\ 2 \\ 2 \end{array} \right\}$	$\left\{ \begin{array}{c} 1 \\ 1 \\ 1 \end{array} \right\}$	$\left\{ \begin{array}{c} -1 \\ 0 \\ +1 \end{array} \right\}$	$\left\{ \begin{array}{c} +\frac{1}{2} \text{ or } -\frac{1}{2} \\ +\frac{1}{2} \text{ or } -\frac{1}{2} \\ +\frac{1}{2} \text{ or } -\frac{1}{2} \end{array} \right\}$	$\left. \begin{array}{l} 2p_x^1 \\ 2p_y^1 \\ 2p_z^1 \end{array} \right\} \text{ or } 2p^3$

EXAMPLE 4-9 Electron Configurations and Quantum Numbers

Write an acceptable set of four quantum numbers for each electron in a chlorine atom.

Plan

Chlorine is element number 17. Its first seven electrons have the same quantum numbers as those of nitrogen in Example 4-8. Electrons 8, 9, and 10 complete the filling of the $2p$ subshell ($n = 2$, $\ell = 1$) and therefore also the second energy level. Electrons 11 through 17 fill the $3s$ subshell ($n = 3$, $\ell = 0$) and partially fill the $3p$ subshell ($n = 3$, $\ell = 1$).

Solution

Electron	n	ℓ	m_ℓ	m_s	e^- Configuration
1, 2	1	0	0	$\pm\frac{1}{2}$	$1s^2$
3, 4	2	0	0	$\pm\frac{1}{2}$	$2s^2$
5–10	$\left\{ \begin{array}{c} 2 \\ 2 \\ 2 \end{array} \right\}$	$\left\{ \begin{array}{c} 1 \\ 1 \\ 1 \end{array} \right\}$	$\left\{ \begin{array}{c} -1 \\ 0 \\ +1 \end{array} \right\}$	$\left\{ \begin{array}{c} \pm\frac{1}{2} \\ \pm\frac{1}{2} \\ \pm\frac{1}{2} \end{array} \right\}$	$2p^6$
11, 12	3	0	0	$\pm\frac{1}{2}$	$3s^2$
13–17	$\left\{ \begin{array}{c} 3 \\ 3 \\ 3 \end{array} \right\}$	$\left\{ \begin{array}{c} 1 \\ 1 \\ 1 \end{array} \right\}$	$\left\{ \begin{array}{c} -1 \\ 0 \\ +1 \end{array} \right\}$	$\left\{ \begin{array}{c} \pm\frac{1}{2} \\ \pm\frac{1}{2} \\ +\frac{1}{2} \text{ or } -\frac{1}{2}^* \end{array} \right\}$	$3p^5$

*The $3p$ orbital with only a single electron can be any one of the set, not necessarily the one with $m_\ell = +1$.

You should now work Exercises 118 and 122.

STOP & THINK

Apply the rules for quantum numbers (see Section 4-16), and remember the Aufbau order of energies (see Figures 4-30 and 4-31).

4-19 The Periodic Table and Electron Configurations

In this section, we will view the *periodic table* (see Section 4-10) from a modern, much more useful perspective—as a systematic representation of the electron configurations of the elements. In the periodic table, elements are arranged in blocks based on the kinds of atomic orbitals that are being filled (Figure 4-32). The periodic tables in this text are divided into “A” and “B” groups. The A groups contain elements in which *s* and *p* orbitals are being filled. Elements within any particular A group have similar electron configurations and chemical properties, as we shall see in the next chapter. The B groups include the transition metals in which there are one or two electrons in the *s* orbital of the outermost occupied shell, and the *d* orbitals, one shell smaller, are being filled.

Lithium, sodium, and potassium, elements of the leftmost column of the periodic table (Group 1A), have a single electron in their outermost *s* orbital (ns^1). Beryllium and magnesium, of Group 2A, have two electrons in their outermost shell, ns^2 , while boron and aluminum (Group 3A) have three electrons in their outermost shell, ns^2np^1 . Similar observations can be made for other A group elements.

The electron configurations of the A group elements and the noble gases can be predicted reliably from Figures 4-30 and 4-31. However, there are some more pronounced irregularities in the B groups below the fourth period. In the heavier B group elements, the higher energy subshells in different principal shells have energies that are very nearly equal (see Figure 4-31). It is easy for an electron to jump from one orbital to another of nearly the same energy, even in a different set. This is because the orbital energies are *perturbed* (changed slightly) as the nuclear charge changes, and an extra electron is added in

► A newer IUPAC system numbers the columns in the periodic table from 1 to 18 for the *s*-, *d*-, and *p*-block elements. This is shown in most of the periodic tables in this book in parentheses under the older system, which uses a number plus A or B. Some chemists use the still older system of a Roman numeral plus A or B.

Group	1A	2A	3B		4B	5B	6B	7B	8B	1B	2B	3A	4A	5A	6A	7A	8A															
	(1)	(2)	(3)		(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)													
Period 1	1 H 1s																	2 He 1s														
2	3 Li 2s	4 Be 2s											5 B 2p	6 C 2p	7 N 2p	8 O 2p	9 F 2p	10 Ne 2p														
3	11 Na 3s	12 Mg 3s											13 Al 3p	14 Si 3p	15 P 3p	16 S 3p	17 Cl 3p	18 Ar 3p														
4	19 K 4s	20 Ca 4s	21 Sc 4s		22 Ti 3d	23 V 3d	24 Cr 3d	25 Mn 3d	26 Fe 3d	27 Co 3d	28 Ni 3d	29 Cu 3d	30 Zn 3d	31 Ga 4p	32 Ge 4p	33 As 4p	34 Se 4p	35 Br 4p	36 Kr 4p													
5	37 Rb 5s	38 Sr 5s	39 Y 5s		40 Zr 4d	41 Nb 4d	42 Mo 4d	43 Tc 4d	44 Ru 4d	45 Rh 4d	46 Pd 4d	47 Ag 4d	48 Cd 4d	49 In 5p	50 Sn 5p	51 Sb 5p	52 Te 5p	53 I 5p	54 Xe 5p													
6	55 Cs 6s	56 Ba 6s	57 La 6s	58 Ce 4f	59 Pr 4f	60 Nd 4f	61 Pm 4f	62 Sm 4f	63 Eu 4f	64 Gd 4f	65 Tb 4f	66 Dy 4f	67 Ho 4f	68 Er 4f	69 Tm 4f	70 Yb 4f	71 Lu 4f	72 Hf 5d	73 Ta 5d	74 W 5d	75 Re 5d	76 Os 5d	77 Ir 5d	78 Pt 5d	79 Au 5d	80 Hg 5d	81 Tl 6p	82 Pb 6p	83 Bi 6p	84 Po 6p	85 At 6p	86 Rn 6p
7	87 Fr 7s	88 Ra 7s	89 Ac 7s	90 Th 5f	91 Pa 5f	92 U 5f	93 Np 5f	94 Pu 5f	95 Am 5f	96 Cm 5f	97 Bk 5f	98 Cf 5f	99 Es 5f	100 Fm 5f	101 Md 5f	102 No 5f	103 Lr 5f	104 Rf 6d	105 Db 6d	106 Sg 6d	107 Bh 6d	108 Hs 6d	109 Mt 6d	110 Ds 6d	111 Rg 6d	112 Cn 6d	113 Uut 7p	114 Fl 7p	115 Uup 7p	116 Lv 7p	117 Uus 7p	118 Uuo 7p

Figure 4-32 A periodic table colored to show the kinds of atomic orbitals (subshells) being filled and the symbols of blocks of elements. The electronic structures of the A group elements are quite regular and can be predicted from their positions in the periodic table, but many exceptions occur in the *d* and *f* blocks. The colors in this figure are the same as those in Figure 4-29.

Hydrogen and helium are shown here in their usual positions in the periodic table. These may seem somewhat unusual based just on their electron configurations. We should remember, however, that the first shell ($n = 1$) can hold a maximum of only two electrons. This shell is entirely filled in helium, so He behaves as a noble gas, and we put it in the column with the other noble gases (Group 8A). Hydrogen has one electron that is easily lost, like the alkali metals (Group 1A), so we put it in Group 1A even though it is not a metal. Furthermore, hydrogen is one electron short of a noble gas configuration (He), so we could also place it with the other such elements in Group 7A.

EXAMPLE 4-10 Electron Configurations

Use Table 4-9 to determine the electron configurations of (a) magnesium, Mg; (b) germanium, Ge; and (c) molybdenum, Mo.

Plan

We will use the electron configurations indicated in Table 4-9 for each group. Each *period* (row) begins filling a new shell (new value of n). Elements to the right of the d orbital block have the d orbitals in the $(n - 1)$ shell already filled. We often find it convenient to collect all sets of orbitals with the same value of n together, to emphasize the number of electrons in the *outermost* shell, that is, the shell with the highest value of n .

Solution

- (a) Magnesium, Mg, is in Group 2A, which has the general configuration s^2 ; it is in Period 3 (third row). The last filled noble gas configuration is that of neon, or [Ne]. The electron configuration of Mg is [Ne] $3s^2$.
- (b) Germanium, Ge, is in Group 4A, for which Table 4-9 shows the general configuration s^2p^2 . It is in Period 4 (the fourth row), so we interpret this as $4s^24p^2$. The last filled noble gas configuration is that of argon, Ar, accounting for 18 electrons. In addition, Ge lies beyond the d orbital block, so we know that the $3d$ orbitals are completely filled. The electron configuration of Ge is [Ar] $4s^23d^{10}4p^2$ or [Ar] $3d^{10}4s^24p^2$.
- (c) Molybdenum, Mo, is in Group 6B, with the general configuration d^5s^1 ; it is in Period 5, which begins with $5s$ and is beyond the noble gas krypton. The electron configuration of Mo is [Kr] $5s^14d^5$ or [Kr] $4d^55s^1$. The electron configuration of molybdenum is analogous to that of chromium, Cr, the element just above it. The configuration of Cr was discussed in Section 4-18 as one of the exceptions to the Aufbau order of filling.

You should now work Exercise 120.

► Although the $4s$ orbital usually fills before the $3d$, most chemists will understand and accept either of the answers shown for the electron configurations of Ge and Mo. The same holds for the configurations of other elements.

► A more complete listing of electron configurations is given in Appendix B.

going from one element to the next. This phenomenon gives rise to other irregularities that are analogous to those seen for Cr and Cu, described earlier.

We can extend the information in Figure 4-32 to indicate the electron configurations that are represented by each *group* (column) of the periodic table. Table 4-9 shows this interpretation of the periodic table, along with the most important exceptions. We can use this interpretation of the periodic table to write, quickly and reliably, the electron configurations for elements.

EXAMPLE 4-11 Unpaired Electrons

Determine the number of unpaired electrons in an atom of tellurium, Te.

Plan

Te is in Group 6A in the periodic table, which tells us that its configuration is s^2p^4 . All other shells are completely filled, so they contain only paired electrons. We need only to find out how many unpaired electrons are represented by s^2p^4 .

Solution

The notation s^2p^4 is a short representation for $s \uparrow\downarrow p \uparrow\downarrow \uparrow \uparrow$. This shows that an atom of Te contains two unpaired electrons.

You should now work Exercises 126 and 128.

STOP & THINK

Remember that electrons occupy a set of equivalent orbitals (a given subshell) *singly* before they pair (Hund's Rule).

Table 4-9 The *s*, *p*, *d*, and *f* Blocks of the Periodic Table*

		GROUPS																												
		1A	2A	3B					4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A							
		(1)	(2)	(3)					(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)							
		s orbital block																				p orbital block						s ²		
		s ¹	s ²																									s ²		
n = 1		1 H																										2 He		
n = 2		3 Li	4 Be																											
n = 3		11 Na	12 Mg																											
n = 4		19 K	20 Ca	21 Sc																										
n = 5		37 Rb	38 Sr	39 Y																										
n = 6		55 Cs	56 Ba	57 La	58 Ce	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn									
n = 7		87 Fr	88 Ra	89 Ac	90 Th	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo									
n = 6	Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	4f subshell														
n = 7	Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	5f subshell														

* n is the principal quantum number. The d^1s^2 , d^2s^2 , ... designations represent *known* configurations. They refer to $(n - 1)d$ and ns orbitals. Several exceptions to the d -block configurations are indicated.

The periodic table has been described as “the chemist’s best friend.” Chemical reactions involve loss, gain, or sharing of electrons. In this chapter, we have seen that the fundamental basis of the periodic table is that it reflects similarities and trends in electron configurations. It is easy to use the periodic table to determine many important aspects of electron configurations of atoms. Practice until you can use the periodic table with confidence to answer many questions about electron configurations. As we continue our study, we will learn many other useful ways to interpret the periodic table. We should always keep in mind that the many trends in chemical and physical properties that we correlate with the periodic table are ultimately based on the trends in electron configurations.

4-20 Paramagnetism and Diamagnetism

Substances that contain unpaired electrons are weakly *attracted* into magnetic fields and are said to be **paramagnetic**. By contrast, those in which all electrons are paired are very weakly repelled by magnetic fields and are called **diamagnetic**. The magnetic effect can be measured by hanging a test tube full of a substance on a balance by a long thread and suspending it above the gap of an electromagnet (Figure 4-33). When the current is switched on, a paramagnetic substance such as copper(II) sulfate is pulled into the strong field. The

► Both paramagnetism and diamagnetism are hundreds to thousands of times weaker than *ferromagnetism*, the effect seen in iron bar magnets.

Unless otherwise noted, all content on this page is © Cengage Learning.

Courtesy of Dr. Andre Geim, Manchester University



A live frog suspended in an extremely strong magnetic field (16 tesla) demonstrating the diamagnetic repulsion effect.

paramagnetic attraction per mole of substance can be measured by weighing the sample before and after energizing the magnet. The paramagnetism per mole increases with increasing number of unpaired electrons per formula unit. Many transition metals and ions have one or more unpaired electrons and are paramagnetic.

Iron, cobalt, and nickel are the only *free* elements that exhibit **ferromagnetism**. This property is much stronger than paramagnetism; it allows a substance to become permanently magnetized when placed in a magnetic field. This happens as randomly oriented electron spins align themselves with an applied field. To exhibit ferromagnetism, the atoms must be within the proper range of sizes so that unpaired electrons on adjacent atoms can interact cooperatively with one another, but not to the extent that they pair. Experimental evidence suggests that in ferromagnets, atoms cluster together into *domains* that contain large numbers of atoms in fairly small volumes. The atoms within each domain interact cooperatively with one another to generate ferromagnetism.

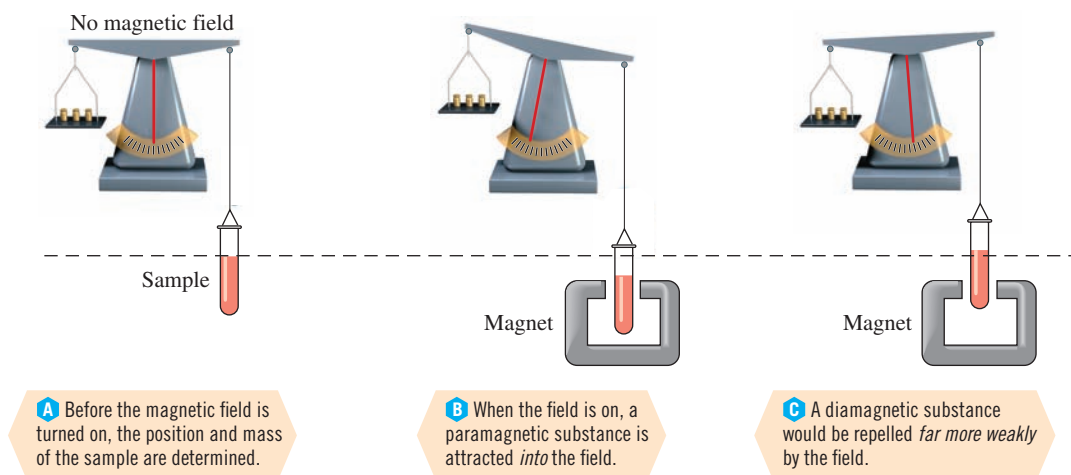


Figure 4-33 Diagram of an apparatus for measuring the paramagnetism of a substance. The tube contains a measured amount of the substance, often in solution.

KEY TERMS

Absorption spectrum The spectrum associated with absorption of electromagnetic radiation by atoms (or other species) resulting from transitions from lower to higher electronic energy states.

Alkali metals Elements of Group 1A in the periodic table, except hydrogen.

Alkaline earth metals Group 2A elements in the periodic table.

Alpha- (α -) particle A helium ion with a 2+ charge; an assembly of two protons and two neutrons.

amu See *Atomic mass unit*.

Angular momentum quantum number (ℓ) The quantum mechanical solution to a wave equation that designates the subshell, or set of orbitals (*s, p, d, f*), within a given main shell in which an electron resides.

Anode In a cathode-ray tube, the positive electrode.

Atomic mass unit (amu) An arbitrary mass unit defined to be exactly one twelfth the mass of the carbon-12 isotope.

Atomic mass (weight) Weighted average of the masses of the constituent isotopes of an element; the relative mass of atoms of different elements.

Atomic number The integral number of protons in the nucleus; defines the identity of an element.

Atomic orbital The region or volume in space in which the probability of finding electrons is highest.

Aufbau (“building up”) Principle A guide for predicting the order in which electrons fill subshells and shells in atoms.

Balmer–Rydberg equation An empirical equation that relates wavelengths in the hydrogen emission spectrum to simple integers.

Canal ray A stream of positively charged particles (cations) that moves toward the negative electrode in a cathode-ray tube; observed to pass through canals (holes) in the negative electrode.

Cathode In a cathode-ray tube, the negative electrode.

Cathode ray The beam of electrons going from the negative electrode toward the positive electrode in a cathode-ray tube.

Cathode-ray tube A closed glass tube containing a gas under low pressure, with electrodes near the ends and a luminescent screen at the end near the positive electrode; produces cathode rays when high voltage is applied.

Chemical periodicity The variation in properties of elements with their positions in the periodic table.

Continuous spectrum A spectrum that contains all wavelengths in a specified region of the electromagnetic spectrum.

***d* orbitals** Beginning in the third shell, a set of five degenerate orbitals per shell, higher in energy than *s* and *p* orbitals in the same shell.

Degenerate orbitals Two or more orbitals that have the same energy.

Diamagnetism *Weak* repulsion by a magnetic field; associated with all electrons in an atom, molecule, or substance being paired.

Electromagnetic radiation Energy that is propagated by means of electric and magnetic fields that oscillate in directions perpendicular to the direction of travel of the energy.

Electron A subatomic particle having a mass of 0.00054858 amu and a charge of $1-$.

Electron configuration The specific distribution of electrons in the atomic orbitals of atoms and ions.

Electron transition The transfer of an electron from one energy level to another.

Emission spectrum The spectrum associated with emission of electromagnetic radiation by atoms (or other species) resulting from electron transitions from higher to lower energy states.

Excited state Any energy state other than the ground state of an atom, ion, or molecule.

***f* orbitals** Beginning in the fourth shell, a set of seven degenerate orbitals per shell, higher in energy than *s*, *p*, and *d* orbitals in the same shell.

Ferromagnetism The property that allows a substance to become permanently magnetized when placed in a magnetic field; exhibited by iron, cobalt, and nickel and some of their alloys.

Frequency (ν) The number of crests of a wave that pass a given point per unit time.

Fundamental particles Subatomic particles of which all matter is composed; protons, electrons, and neutrons are fundamental particles.

Ground state The lowest energy state or most stable state of an atom, molecule, or ion.

Group (family) The elements in a vertical column of the periodic table.

Halogens Elements of Group 7A in the periodic table.

Heisenberg Uncertainty Principle It is impossible to determine accurately both the momentum and position of an electron simultaneously.

Hund's Rule Each orbital of a given subshell is occupied by a single electron before pairing begins. See *Aufbau Principle*.

Isotopes Two or more forms of atoms of the same element with different masses; that is, atoms containing the same number of protons but different numbers of neutrons.

Line spectrum An atomic emission or absorption spectrum.

Magnetic quantum number (m_l) Quantum mechanical solution to a wave equation that designates the particular orbital within a given subshell (*s*, *p*, *d*, *f*) in which an electron resides. The p_x , p_y , and p_z orbitals have different magnetic quantum numbers.

Mass number The integral sum of the numbers of protons and neutrons in an atom.

Mass spectrometer An instrument that measures the charge-to-mass ratios of charged particles.

Metal An element below and to the left of the stepwise division (metalloids) of the periodic table; about 80% of the known elements are metals.

Metalloids Elements with properties intermediate between metals and nonmetals: B, Si, Ge, As, Sb, Te, and At.

Natural radioactivity Spontaneous decomposition of an atom.

Neutron A subatomic nuclear particle having a mass of 1.0087 amu and no charge.

Noble (rare) gases Elements of Group 8A in the periodic table.

Nonmetals Elements above and to the right of the metalloids in the periodic table.

Nucleus The very small, very dense, positively charged center of an atom, consisting of protons and neutrons (except for ^1H , which has no neutrons).

Nuclide symbol The symbol for an atom, ^A_ZE , in which *E* is the symbol for an element, *Z* is its atomic number, and *A* is its mass number.

Orbital Each allowed wave description of a stable state for an electron in an atom; a region of space in which the probability of finding an electron is high.

***p* orbitals** Beginning with the second shell, a set of three degenerate, mutually perpendicular, equal-arm, dumbbell-shaped atomic orbitals per shell.

Paired electrons Two electrons with opposite m_s values in the same orbital ($\uparrow\downarrow$). Also known as *spin-paired electrons*.

Paramagnetism Attraction toward a magnetic field, stronger than diamagnetism, but still very weak compared with ferromagnetism; due to presence of unpaired electrons.

Pauli Exclusion Principle No two electrons in the same atom may have identical sets of four quantum numbers.

Period The elements in a horizontal row of the periodic table.

Periodic law The properties of the elements are periodic functions of their atomic numbers.

Periodic table An arrangement of elements in order of increasing atomic number that also emphasizes periodicity.

Periodicity Regular periodic variations of properties of elements with atomic number (and position in the periodic table).

Photoelectric effect Emission of an electron from the surface of a metal, caused by impinging electromagnetic radiation of certain minimum energy; the resulting current increases with increasing intensity of radiation.

Photon A "packet" of light or electromagnetic radiation; also called a quantum of light.

Principal quantum number (*n*) The quantum mechanical solution to a wave equation that designates the main shell, or energy level, in which an electron resides.

Proton A subatomic particle having a mass of 1.0073 amu and a charge of $1+$, found in the nuclei of atoms.

Quantum A "packet" of energy. See *Photon*.

Quantum mechanics A mathematical method of treating particles on the basis of quantum theory, which assumes that energy (of small particles) is not infinitely divisible.

Quantum numbers Numbers that describe the energies of electrons in atoms; they are derived from quantum mechanical treatment.

Radiant energy See *Electromagnetic radiation*.

***s* orbital** A spherically symmetrical atomic orbital; one per shell.

Spectral line Any of a number of lines corresponding to definite wavelengths in an atomic emission or absorption spectrum; these lines represent the energy difference between two energy levels.

Spectrum Display of component wavelengths of electromagnetic radiation.

Spin quantum number (m_s) The quantum mechanical solution to a wave equation that indicates the relative spins of electrons ("spin up" and "spin down").

Wavelength (λ) The distance between two identical points of a wave.

Unless otherwise noted, all content on this page is © Cengage Learning.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Particles and the Nuclear Atom

1. List the three fundamental particles of atoms, and indicate the mass and charge associated with each.
2. In the oil-drop experiment, how did Millikan know that none of the oil droplets he observed were ones that had a deficiency of electrons rather than an excess?
3. ● How many electrons carry a total charge of 1.00 coulomb?
4. (a) How do we know that canal rays have charges opposite in sign to cathode rays? What are canal rays? (b) Why are cathode rays from all samples of gases identical, whereas canal rays are not?
5. ▲ The following data are measurements of the charges on oil droplets using an apparatus similar to that used by Millikan:

$13.458 \times 10^{-19} \text{ C}$	$15.373 \times 10^{-19} \text{ C}$
$17.303 \times 10^{-19} \text{ C}$	$15.378 \times 10^{-19} \text{ C}$
$17.308 \times 10^{-19} \text{ C}$	$28.844 \times 10^{-19} \text{ C}$
$11.545 \times 10^{-19} \text{ C}$	$19.214 \times 10^{-19} \text{ C}$

Each should be a whole-number ratio of some fundamental charge. Using these data, determine the largest possible value of the fundamental charge.

6. ▲ Suppose we discover a new positively charged particle, which we call the “whizatron.” We want to determine its charge. (a) What modifications would we have to make to the Millikan oil-drop apparatus to carry out the corresponding experiment on whizatrons? (b) In such an experiment, we observe the following charges on five different droplets:

$4.88 \times 10^{-19} \text{ C}$	$8.53 \times 10^{-19} \text{ C}$
$6.10 \times 10^{-19} \text{ C}$	$7.32 \times 10^{-19} \text{ C}$
$2.44 \times 10^{-19} \text{ C}$	

What is the largest possible value of the charge on the whizatron?

7. Outline Rutherford’s contribution to understanding the nature of atoms.
8. Why was Rutherford so surprised that some of the α -particles were scattered backward in the gold foil experiment?
9. Summarize Moseley’s contribution to our knowledge of the structure of atoms.
10. The approximate radius of a hydrogen atom is 0.0529 nm, and that of a proton is $1.5 \times 10^{-15} \text{ m}$. Assuming both the hydrogen atom and the proton to be spherical, calculate the fraction of the space in an atom of hydrogen that is occupied by the nucleus. $V = (4/3)\pi r^3$ for a sphere.
11. The approximate radius of a neutron is $1.5 \times 10^{-15} \text{ m}$, and the mass is $1.675 \times 10^{-27} \text{ kg}$. Calculate the density of a neutron. $V = (4/3)\pi r^3$ for a sphere.

Atomic Composition, Isotopes, and Atomic Weights

12. ● Arrange the following in order of increasing ratio of charge to mass: $^{12}\text{C}^+$, $^{12}\text{C}^{2+}$, $^{14}\text{N}^+$, $^{14}\text{N}^{2+}$.
13. ● ▲ Refer to Exercise 12. Suppose all of these high-energy ions are present in a mass spectrometer. For which one will its path be changed (a) the most and (b) the least by increasing the external magnetic field? Which of the ions would take (c) the longest time and (d) the shortest time to travel a given distance in a time-of-flight mass spectrometer?
14. ● Estimate the percentage of the total mass of a ^{58}Ni atom that is due to (a) electrons, (b) protons, and (c) neutrons by *assuming* that the mass of the atom is simply the sum of the masses of the appropriate numbers of subatomic particles.
15. ● (a) How are isotopic abundances determined experimentally? (b) How do the isotopes of a given element differ?
16. ● Clearly define and provide examples that illustrate the meaning of each: (a) atomic number; (b) isotope; (c) mass number; (d) nuclear charge.
17. ● Write the composition of one atom of each of the three isotopes of silicon: ^{28}Si , ^{29}Si , ^{30}Si .
18. ● Write the composition of one atom of each of the four isotopes of strontium: ^{84}Sr , ^{86}Sr , ^{87}Sr , ^{88}Sr .
19. ● Complete Chart A on the next page for neutral atoms.
20. ● Complete Chart B on the next page for neutral atoms.
21. ▲ Prior to 1962, the atomic weight scale was based on the assignment of an atomic weight of exactly 16 amu to the *naturally occurring* mixture of oxygen. The atomic weight of nickel is 58.6934 amu on the carbon-12 scale. What would it have been on the older scale?
22. ● Determine the number of protons, neutrons, and electrons in each of the following species: (a) ^{24}Mg ; (b) ^{51}V ; (c) ^{91}Zr ; (d) ^{27}Al ; (e) $^{65}\text{Zn}^{2+}$; (f) $^{108}\text{Ag}^+$.
23. ● Determine the number of protons, neutrons, and electrons in each of the following species: (a) ^{52}Cr ; (b) ^{112}Cd ; (c) $^{137}\text{Ba}^{2+}$; (d) $^{63}\text{Cu}^+$; (e) $^{56}\text{Fe}^{2+}$; (f) $^{55}\text{Fe}^{3+}$.
24. ● What is the symbol of the species composed of each of the following sets of subatomic particles? (a) 24p, 28n, 24e; (b) 20p, 20n, 20e; (c) 33p, 42n, 33e; (d) 53p, 74n, 53e.
25. ● What is the symbol of the species composed of each of the following sets of subatomic particles? (a) 94p, 150n, 94e; (b) 79p, 118n, 76e; (c) 34p, 45n, 34e; (d) 56p, 80n, 56e.
26. The listed atomic weight of gallium is 69.723 amu. Gallium has two stable isotopes, both of which are used in nuclear medicine. These two stable isotopes have the following masses: ^{69}Ga , 68.925580; ^{71}Ga , 70.9247005. Calculate the percent of each isotope in naturally occurring gallium.

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

Chart A

Kind of Atom	Atomic Number	Mass Number	Isotope	Number of Protons	Number of Electrons	Number of Neutrons
			^{21}Ne			
potassium		39				
	14	28				
		202		80		

Chart B

Kind of Atom	Atomic Number	Mass Number	Isotope	Number of Protons	Number of Electrons	Number of Neutrons
cobalt						32
			^{11}B			
					25	30
		182			78	

27. The atomic weight of rubidium is 85.4678 amu. The two naturally occurring isotopes of rubidium have the following masses: ^{85}Rb , 84.9118 amu; ^{87}Rb , 86.9092 amu. Calculate the percent of each isotope in naturally occurring rubidium.
28. Strontium has four isotopes with the following masses: 83.9134 amu (0.56%), 85.9094 amu (9.86%), 86.9089 amu (7.00%), and 87.9056 (82.58%). Calculate the atomic mass of strontium.
29. What is the atomic weight of a hypothetical element that consists of the following isotopes in the indicated relative abundances?

Isotope	Isotopic Mass (amu)	% Natural Abundance
1	94.9	12.4
2	95.9	73.6
3	97.9	14.0

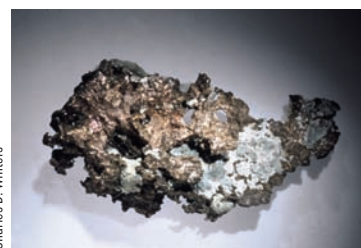
30. Naturally occurring iron consists of four isotopes with the abundances indicated here. From the masses and relative abundances of these isotopes, calculate the atomic weight of naturally occurring iron.

Isotope	Isotopic Mass (amu)	% Natural Abundance
^{54}Fe	53.9396	5.82
^{56}Fe	55.9349	91.66
^{57}Fe	56.9354	2.19
^{58}Fe	57.9333	0.33

31. Calculate the atomic weight of nickel from the following information.

Isotope	Isotopic Mass (amu)	% Natural Abundance
^{58}Ni	57.9353	68.08
^{60}Ni	59.9308	26.22
^{61}Ni	60.9311	1.14
^{62}Ni	61.9283	3.63
^{64}Ni	63.9280	0.93

32. The atomic weight of copper is 63.546 amu. The two naturally occurring isotopes of copper have the following masses: ^{63}Cu , 62.9298 amu; ^{65}Cu , 64.9278 amu. Calculate the percent of ^{63}Cu in naturally occurring copper.



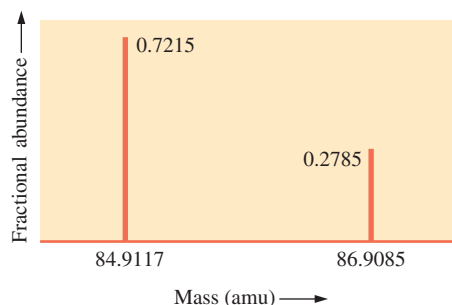
Charles D. Winters

Native copper

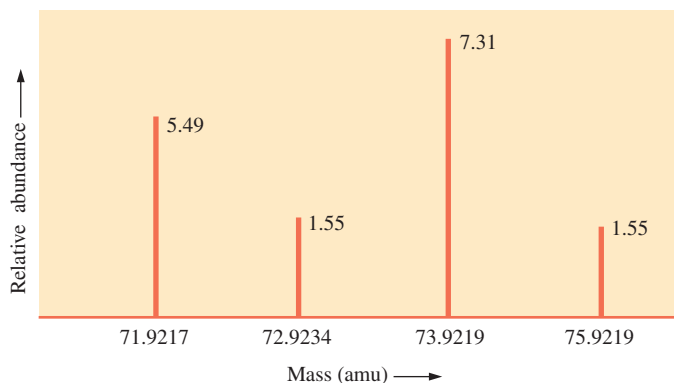
33. Silver consists of two naturally occurring isotopes: ^{107}Ag , which has a mass of 106.90509 amu, and ^{109}Ag , which has a mass of 108.9047 amu. The atomic weight of silver is 107.8682 amu. Determine the percent abundance of each isotope in naturally occurring silver.



34. Refer to Table 4-3 *only* and calculate the atomic weights of oxygen and chlorine. Do your answers agree with the atomic weights given in that table?
35. The following is a mass spectrum of the 1+ charged ions of an element. Calculate the atomic weight of the element. What is the element?



36. Suppose you measure the mass spectrum of the 1+ charged ions of germanium, atomic weight 72.61 amu. Unfortunately, the mass spectrometer malfunctions at the beginning and again at the end of your experiment. You obtain only the following spectrum, which *may or may not be complete*. From the information given here, can you tell whether one of the germanium isotopes is missing? If one is missing, at which end of the plot should it appear?



37. Calculate the atomic weight of silicon using the following data for the percent natural abundance and mass of each isotope: 92.23% ^{28}Si (27.9769 amu); 4.67% ^{29}Si (28.9765 amu); 3.10% ^{30}Si (29.9738 amu).



Silicon

38. Calculate the atomic weight of chromium using the following data for the percent natural abundance and mass of each isotope: 4.35% ^{50}Cr (49.9461 amu); 83.79% ^{52}Cr (51.9405 amu); 9.50% ^{53}Cr (52.9406 amu); 2.36% ^{54}Cr (53.9389 amu).

The Periodic Table

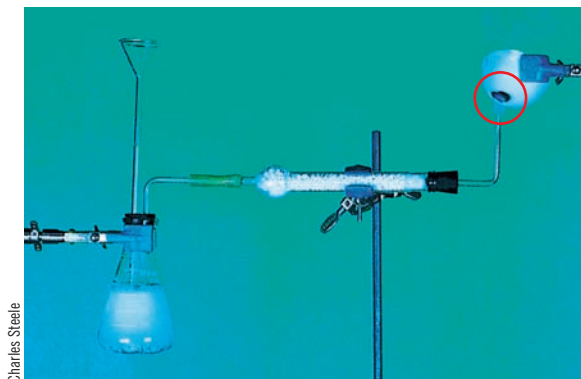
39. State the periodic law. What does it mean?
40. What was Mendeleev's contribution to the construction of the modern periodic table?
41. Consult a handbook of chemistry or a suitable website, and look up melting points of the elements of Periods 2 and 3. Show that melting point is a property that varies periodically for these elements.
42. Mendeleev's periodic table was based on increasing atomic weight. Argon has a higher atomic weight than potassium, yet in the modern table argon appears before potassium. Explain how this can be.
43. Estimate the density of antimony from the following densities (g/cm^3): As, 5.72; Bi, 9.8; Sn, 7.30; Te, 6.24. Show how you arrived at your answer. Using a reference other than your textbook, look up the density of antimony. How does your predicted value compare with the reported value?



Antimony is used to harden the lead in lead storage batteries.

44. Estimate the density of selenium from the following densities (g/cm^3): S, 2.07; Te, 6.24; As, 5.72; Br, 3.12. Show how you arrived at your answer. Using a reference other than your textbook, look up the density of selenium. How does your predicted value compare with the reported value?
45. Estimate the specific heat of antimony from the following specific heats ($\text{J}/\text{g} \cdot ^\circ\text{C}$): As, 0.34; Bi, 0.14; Sn, 0.23; Te, 0.20. Show how you arrived at your answer.
46. Given the following melting points in $^\circ\text{C}$, estimate the value for CBr_4 : CF_4 , -184 ; CCl_4 , -23 ; CI_4 , 171 (decomposes). Using a reference other than your textbook, look up the melting point of CBr_4 . How does your predicted value compare with the reported value?
47. Calcium and magnesium form the following compounds: CaCl_2 , MgCl_2 , CaO , MgO , Ca_3N_2 , and Mg_3N_2 . Predict the formula for a compound of (a) magnesium and sulfur, (b) barium and bromine.

48. The formulas of some hydrides of second-period representative elements are as follows: BeH_2 , BH_3 , CH_4 , NH_3 , H_2O , HF . A famous test in criminology laboratories for the presence of arsenic (As) involves the formation of arsine, the hydride of arsenic. Predict the formula of arsine.

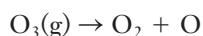


Arsine burns to form a dark spot.

49. Clearly distinguish between the following terms and provide specific examples of each: groups (families) of elements and periods of elements.
50. Write names and symbols for (a) the alkaline earth metals; (b) the Group 4A elements; (c) the Group 2B elements.
51. Write names and symbols for (a) the alkali metals; (b) the noble gases; (c) the Group 4A elements.
52. Clearly and concisely define the following terms and provide examples of each: (a) metals; (b) nonmetals; (c) halogens.

Electromagnetic Radiation

53. Calculate the wavelengths, in meters, of radiation of the following frequencies: (a) $4.80 \times 10^{15} \text{ s}^{-1}$; (b) $1.18 \times 10^{14} \text{ s}^{-1}$; (c) $5.44 \times 10^{12} \text{ s}^{-1}$.
54. Calculate the frequency of radiation of each of the following wavelengths: (a) $8973 \text{ \AA}$; (b) 442 nm ; (c) 4.92 cm ; (d) $4.55 \times 10^{-9} \text{ cm}$.
55. What is the energy of a photon of each of the radiations in Exercise 53? Express your answer in joules per photon. In which regions of the electromagnetic spectrum do these radiations fall?
56. Excited lithium ions emit radiation at a wavelength of 670.8 nm in the visible range of the spectrum. (This characteristic color is often used as a qualitative analysis test for the presence of Li^+ .) Calculate (a) the frequency and (b) the energy of a photon of this radiation. (c) What color is this light?
57. Calculate the energy, in joules per photon, of the red line, $6573 \text{ \AA}$, in the discharge spectrum of atomic calcium.
58. Ozone in the upper atmosphere absorbs ultraviolet radiation, which induces the following chemical reaction:



What is the energy of a $3400\text{-\AA}$ photon that is absorbed? What is the energy of a mole of these photons?

59. During photosynthesis, chlorophyll- α absorbs light of wavelength 440 nm and emits light of wavelength 670 nm . How much energy is available for photosynthesis from the absorption–emission of a mole of photons?



Photosynthesis

60. Alpha Centauri is the star closest to our solar system. It is 4.3 light-years away. How many miles is this? A light year is the distance that light travels (in a vacuum) in one year. Assume that space is essentially a vacuum.

The Photoelectric Effect

61. What evidence supports the idea that electromagnetic radiation is (a) wave-like; (b) particle-like?
62. Describe the influence of frequency and intensity of electromagnetic radiation on the current in the photoelectric effect.
63. Cesium is often used in “electric eyes” for self-opening doors in an application of the photoelectric effect. The amount of energy required to ionize (remove an electron from) a cesium atom is 3.89 electron volts ($1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$). Show by calculation whether a beam of yellow light with wavelength $5830 \text{ \AA}$ would ionize a cesium atom.
64. Refer to Exercise 63. What would be the wavelength, in nanometers, of light with just sufficient energy to ionize a cesium atom? What color would this light be?

Atomic Spectra and the Bohr Theory

65. (a) Distinguish between an atomic emission spectrum and an atomic absorption spectrum. (b) Distinguish between a continuous spectrum and a line spectrum.

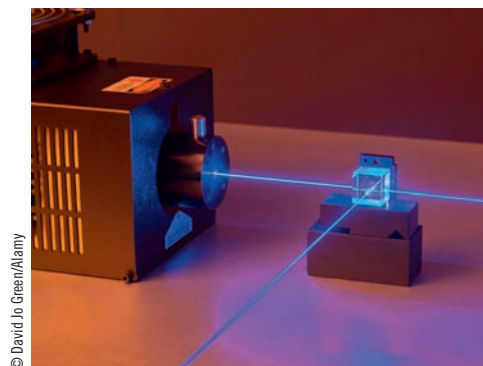


66. ● ▲ Prepare a sketch similar to Figure 4-18b that shows a ground energy state and three excited energy states. Using vertical arrows, indicate the transitions that would correspond to the absorption spectrum for this system.
67. ● Why is the Bohr model of the hydrogen atom referred to as the solar system model?
68. ● ▲ If each atom in one mole of atoms emits a photon of wavelength $5.50 \times 10^3 \text{ \AA}$, how much energy is lost? Express the answer in kJ/mol. As a reference point, burning one mole (16 g) of CH_4 produces 819 kJ of heat.
69. What is the Balmer–Rydberg equation? Why is it called an empirical equation?
70. Hydrogen atoms absorb energy so that the electrons are excited to the energy level $n = 7$. Electrons then undergo these transitions: (1) $n = 7 \rightarrow n = 1$; (2) $n = 7 \rightarrow n = 2$; (3) $n = 2 \rightarrow n = 1$. Which of these transitions will produce the photon with (a) the smallest energy; (b) the highest frequency; (c) the shortest wavelength? (d) What is the frequency of a photon resulting from the transition $n = 6 \rightarrow n = 1$?
71. ▲ Five energy levels of the He atom are given in joules per atom above an *arbitrary* reference energy: (1) 6.000×10^{-19} ; (2) 8.812×10^{-19} ; (3) 9.381×10^{-19} ; (4) 10.443×10^{-19} ; (5) 10.934×10^{-19} . Construct an energy level diagram for He, and find the energy of the photon (a) absorbed for the electron transition from level 1 to level 5 and (b) emitted for the electron transition from level 4 to level 1.
72. The following are prominent lines in the visible region of the emission spectra of the elements listed. The lines can be used to identify the elements. What color is the light responsible for each line? (a) lithium, 4603 $\text{\AA}$; (b) neon, 540.0 nm; (c) calcium, 6573 $\text{\AA}$; (d) potassium, $\nu = 3.90 \times 10^{14} \text{ Hz}$.



73. Hydrogen atoms have an absorption line at 1026 $\text{\AA}$. What is the frequency of the photons absorbed, and what is the energy difference, in joules, between the ground state and this excited state of the atom?

74. An argon laser emits blue light with a wavelength of 488.0 nm. How many photons are emitted by this laser in 2.00 seconds, operating at a power of 515 milliwatts? One watt (a unit of power) is equal to 1 joule/second.



Lasers

The Wave–Particle View of Matter

75. (a) What evidence supports the idea that electrons are particle-like? (b) What evidence supports the idea that electrons are wave-like?
76. (a) What is the de Broglie wavelength of a proton moving at a speed of $2.50 \times 10^7 \text{ m/s}$? The proton mass is $1.67 \times 10^{-24} \text{ g}$. (b) What is the de Broglie wavelength of a stone with a mass of 30.0 g moving at $2.00 \times 10^5 \text{ m/h}$ ($\approx 100 \text{ mph}$)? (c) How do the wavelengths in parts (a) and (b) compare with the typical radii of atoms? (See the atomic radii in Figure 5-1.)
77. What is the wavelength corresponding to a neutron of mass $1.67 \times 10^{-27} \text{ kg}$ moving at 2360 m/s?
78. What is the velocity of an α -particle (a helium nucleus) that has a de Broglie wavelength of 0.529 $\text{\AA}$?

Quantum Numbers and Atomic Orbitals

79. (a) What is a quantum number? What is an atomic orbital? (b) How many quantum numbers are required to specify a single atomic orbital? What are they?
80. How are the possible values for the angular momentum quantum number for a given electron restricted by the value of n ?
81. Without giving the ranges of possible values of the four quantum numbers, n , ℓ , m_ℓ , and m_s , describe briefly what information each one gives.
82. Draw an orbital that has the following quantum numbers: $n = 3$, $\ell = 1$, $m_\ell = -1$, and $m_s = -\frac{1}{2}$.
83. What is the maximum number of electrons in an atom that can have the following quantum numbers? (a) $n = 2$; (b) $n = 3$ and $\ell = 1$; (c) $n = 3$, $\ell = 1$, and $m_\ell = 0$; (d) $n = 3$, $\ell = 1$, $m_\ell = -1$, and $m_s = -\frac{1}{2}$.
84. What is the maximum number of electrons in an atom that can have the following quantum numbers? (a) $n = 3$ and $\ell = 1$; (b) $n = 3$ and $\ell = 2$; (c) $n = 3$, $\ell = 0$ and $m_\ell = -1$; (d) $n = 3$, $\ell = 1$, and $m_\ell = -1$; (e) $n = 3$, $\ell = 1$, $m_\ell = 0$, and $m_s = -\frac{1}{2}$.

85. What are the values of n and ℓ for the following subshells? (a) $1s$; (b) $3s$; (c) $5p$; (d) $3d$; (e) $4f$.
86. (a) How many sublevels are in the third main energy level? (b) Which, if any, of these sublevels contain a set of equivalent orbitals? (c) Sketch, on the same relative scale, at least one orbital from each of these sublevels.
87. (a) How many sublevels are in the second main energy level? (b) Which, if any, of these sublevels contain a set of equivalent orbitals? (c) Sketch, on the same relative scale, at least one orbital from each of these sublevels.
88. How many individual orbitals are there in the third shell? Write out n , ℓ , and m_ℓ quantum numbers for each one, and label each set by the s , p , d , f designations.
89. (a) Write the possible values of ℓ when $n = 4$. (b) Write the allowed number of orbitals (1) with the quantum numbers $n = 3$, $\ell = 1$; (2) with the quantum numbers $n = 2$, $\ell = 1$; (3) with the quantum numbers $n = 3$, $\ell = 1$, $m_\ell = -1$; (4) with the quantum number $n = 1$.
90. What are the possible values for m_ℓ for (a) the p sublevel? (b) the f sublevel? (c) all sublevels where $n = 3$?
91. Write a complete set of quantum numbers (n , ℓ , and m_ℓ) for each of the following orbitals: (a) $5f$; (b) $4d$; and (c) $2s$.
92. How many orbitals correspond to each of the following designations? (a) $3p$; (b) $4p$; (c) $4p_x$; (d) $6d$; (e) $5d$; (f) $5f$; (g) $n = 5$; (h) $7s$.
93. The following incorrect sets of quantum numbers in the order n , ℓ , m_ℓ , m_s are written for paired electrons or for one electron in an orbital. Correct them, assuming the n values are correct. (a) $1, 0, 0, +\frac{1}{2}, +\frac{1}{2}$; (b) $2, 2, 1, \frac{1}{2}$; (c) $3, 2, 3, \pm\frac{1}{2}$; (d) $3, 1, 2, +\frac{1}{2}$; (e) $2, 1, -1, 0$; (f) $3, -0, -1, -\frac{1}{2}$.
94. (a) How are a $1s$ orbital and a $2s$ orbital in an atom similar? How do they differ? (b) How are a $3p_x$ orbital and a $2p_y$ orbital in an atom similar? How do they differ?
99. Explain why each of the following ground state configurations is incorrect, and correct it.
 (a) $\text{Ca } 1s \uparrow\downarrow 2s \uparrow\downarrow 2p \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow 3s \uparrow 3p \uparrow$
 (b) $\text{V } [\text{Ar}] 3d \uparrow \uparrow \uparrow \uparrow \uparrow$
 (c) $\text{F } 1s \uparrow\downarrow 2s \uparrow 2p \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$
100. A neutral atom has two electrons with $n = 1$, eight electrons with $n = 2$, eight electrons with $n = 3$, and two electrons with $n = 4$. Assume this element is in its ground state configuration.
 (a) What are the atomic number, symbol, and name of this element?
 (b) In which period of the periodic table does this element appear?
 (c) In which group of the periodic table does this element appear?
 (d) What is the total number of s electrons in this atom?
 (e) What is the total number of p electrons in this atom?
 (f) What is the total number of d electrons in this atom?
101. A neutral atom has two electrons with $n = 1$, eight electrons with $n = 2$, sixteen electrons with $n = 3$, and two electrons with $n = 4$. Assume this element is in its ground state configuration.
 (a) What are the atomic number, symbol, and name of this element?
 (b) In which period of the periodic table does this element appear?
 (c) In which group of the periodic table does this element appear?
 (d) What is the total number of s electrons in this atom?
 (e) What is the total number of p electrons in this atom?

Electron Configurations and the Periodic Table

You should be able to use the positions of elements in the periodic table to answer the exercises in this section.

95. Draw representations of ground state electron configurations using the orbital notation ($\uparrow\downarrow$) for the following elements. (a) F; (b) V; (c) Br; (d) Rh.
96. Draw representations of ground state electron configurations using the orbital notation ($\uparrow\downarrow$) for the following elements. (a) P; (b) Ni; (c) Ga; (d) Cd.
97. Determine the number of electrons in the outer occupied shell of each of the following elements, and indicate the principal quantum number of that shell. (a) Na; (b) Si; (c) Sr; (d) Ba; (e) Br.
98. Explain why each of the following ground state configurations is incorrect, and correct it.
 (a) $\text{Si } 1s \uparrow\downarrow 2s \uparrow\downarrow 2p \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow 3s \uparrow 3p \uparrow \uparrow \uparrow$
 (b) $\text{Ni } [\text{Ar}] 4s \uparrow 3d \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow$
 (c) $\text{S } [\text{Ne}] 3s \uparrow\downarrow 3p \uparrow\downarrow \uparrow\downarrow$
102. With the help of Appendix B, list the symbols for the first five elements, by atomic number, that have an unpaired electron in an s orbital. Identify the group in which most of these are found in the periodic table.
103. List the elements having an atomic number of 20 or less that have one or more unpaired p orbital electrons. Indicate the group to which each of these elements belongs in the periodic table.
104. Identify the element or elements possible, given only the number of electrons in the outermost shell and the principal quantum number of that shell. (a) 1 electron, first shell; (b) 3 electrons, second shell; (c) 3 electrons, third shell; (d) 2 electrons, seventh shell; (e) 4 electrons, third shell; (f) 8 electrons, fifth shell.
105. Give the ground state electron configurations for the elements of Exercise 95 using shorthand notation—that is, $[\text{He}] 2s^2 2p^6$, and so on.
106. Give the ground state electron configurations for the elements of Exercise 96 using shorthand notation—that is, $[\text{He}] 2s^2 2p^6$, and so on.



- 107.** State the Pauli Exclusion Principle. Would any of the following ground state electron configurations violate this rule: (a) $1s^3$; (b) $1s^22s^22p_x^22p_y^3$; (c) $1s^22s^22p_x^2$; (d) $1s^22s^23s^2$? Explain.
- 108.** State Hund's Rule. Would any of the following ground state electron configurations violate this rule: (a) $1s^2$; (b) $1s^22s^22p_x^2$; (c) $1s^22s^22p_x^12p_y^1$; (d) $1s^22s^12p_x^12p_z^1$; (e) $1s^22s^12p_x^22p_y^12p_z^1$? Explain.
- 109.** ▲ Classify each of the following atomic electron configurations as (i) a ground state, (ii) an excited state, or (iii) a forbidden state: (a) $1s^22p^3$; (b) $[\text{Kr}] 4d^{10}5s^3$; (c) $1s^22s^22p^63s^23p^63d^{12}4s^2$; (d) $1s^22s^22p^63s^23p^62d^1$; (e) $1s^22s^22p^83s^23p^5$.
- 110.** Which of the elements with atomic numbers of 11 or less are paramagnetic when in the ground atomic state?
- 111.** Semiconductor industries depend on such elements as Si, Ga, As, Ge, B, Cd, and S. Write the predicted electron configuration of each element.
- 112.** The manufacture of high-temperature ceramic superconductors depends on such elements as Cu, O, La, Y, Ba, Tl, and Bi. Write the predicted electron configuration of each element. (Consult Appendix B if necessary.)
- 113.** In nature, potassium and sodium are often found together. (a) Write the electron configurations for potassium and for sodium. (b) How are they similar? (c) How do they differ?
- 116.** Find the total number of s , p , and d electrons in each of the following: (a) P; (b) Kr; (c) Ni; (d) Zn; (e) Ti.
- 117.** Write the electron configurations of the Group 2A elements Be, Mg, and Ca (see inside front cover). What similarities do you observe?
- 118.** Construct a table in which you list a possible set of values for the four quantum numbers for each electron in the following atoms in their ground states. (a) Na; (b) O; (c) Ca.
- 119.** Construct a table in which you list a possible set of values for the four quantum numbers for each electron in the following atoms in their ground states. (a) Mg; (b) S; (c) Sc.
- 120.** Draw general electron structures for the A group elements using the $\uparrow\downarrow$ notation, where n is the principal quantum number for the highest occupied energy level.

	ns	np
1A	—	— — —
2A	—	— — —
and so on		
- 121.** Repeat Exercise 120 using ns^xnp^y notation.
- 122.** List n , ℓ , and m_ℓ quantum numbers for the highest energy electron (or one of the highest energy electrons if there are more than one) in the following atoms in their ground



Metallic potassium



Metallic sodium

- 114.** Which elements are represented by the following electron configurations?
- $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
 - $[\text{Kr}] 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^3$
 - $[\text{Kr}] 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 5f^{14} 6s^2 6p^6 7s^2$
 - $[\text{Kr}] 4d^5 5s^2$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
- 115.** Repeat Exercise 114 for
- $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
 - $[\text{Kr}] 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^4$
 - $1s^2 2s^2 2p^6 3s^2 3p^5$
 - $[\text{Kr}] 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2$

	<i>ns</i>	<i>np</i>
1A	—	— — —
2A	—	— — —
and so on		

121. Repeat Exercise 120 using ns^xnp^y notation.
122. List n , ℓ , and m_ℓ quantum numbers for the highest energy electron (or one of the highest energy electrons if there are more than one) in the following atoms in their ground states. (a) Si; (b) Ac; (c) Cl; (d) Pr.
123. List n , ℓ , and m_ℓ quantum numbers for the highest energy electron (or one of the highest energy electrons if there are more than one) in the following atoms in their ground states. (a) Se; (b) Zn; (c) Mg; (d) Pu.
124.  Write the ground state electron configurations for elements A–F.

[illegible]

125.  Repeat Exercise 124 for elements F–J.
126. How many unpaired electrons are in atoms of Na, Ne, Al, Be, Br, As, and Ti?
127. (a) Distinguish between the terms “diamagnetic” and “paramagnetic,” and provide an example that illustrates the meaning of each. (b) How is paramagnetism measured experimentally?
128. Which of the following ions or atoms possess paramagnetic properties? (a) Br; (b) Kr; (c) Ne^+ ; (d) Fe; (e) Br^- .
129. Which of the following ions or atoms possess paramagnetic properties? (a) Cl^- ; (b) Ca^{2+} ; (c) Ca; (d) Ar^- ; (e) Si.

Conceptual Exercises

130. ● The atomic mass of chlorine is reported to be 35.5, yet no atom of chlorine has the mass of 35.5 amu. Explain.
131. Chemists often use the terms “atomic weight” and “atomic mass” interchangeably. Explain why it would be more accurate if, in place of either of these terms, we used the phrase “average atomic mass.”
132. The diameter of an atom is about 100,000 times larger than the diameter of the nucleus of the atom. Suppose an atom is enlarged until its nucleus is the size of a basketball, which has a diameter of 9.39 inches. What would be the diameter of this enlarged atom?
133. Using the electron configurations of the elements, given in Appendix B, and Hund’s Rule, determine which elements have a pair of electrons in every occupied orbital (no singles). Are they about half of the elements, rather small in number, or rather large in number? To what groups of elements do they belong?
134. Draw a three-dimensional representation of each of the following orbitals: (a) $3p_{xy}$; (b) $2s$; (c) $3d_{xy}$; (d) $3d_{z^2}$.
135. ● We often show the shapes of orbitals as drawings. What are some of the limitations of these drawings?
136. An atom in its ground state contains 18 electrons. How many of these electrons are in orbitals with $\ell = 0$ values?
137. Suppose that scientists were to discover a new element, one that has the chemical properties of the noble gases, and positioned directly below radon on the periodic table. Assuming that the g orbitals of the elements preceding it in the period had not yet begun to fill, what would be the atomic number and ground state electron configuration of this new element?
138. For a lithium atom, give (a) its ground state electron configuration; (b) the electron configuration for one of its lowest energy excited states; and (c) an electron configuration for a forbidden or impossible state.
139. Suppose we could excite all of the electrons in a sample of hydrogen atoms to the $n = 6$ level. They would then emit light as they relaxed to lower energy states. Some atoms might undergo the transition $n = 6$ to $n = 1$, and others might go from $n = 6$ to $n = 5$, then from $n = 5$ to $n = 4$, and so on. How many lines would we expect to observe in the resulting emission spectrum?
140. Examine each of the following statements. What is incorrect about each statement? How can each statement be changed to make it a correct statement?
- A hydrogen atom has one energy level.
 - A lithium atom has three electrons, two in the $1s$ sublevel and one in the $2p$ sublevel.
 - The angular momentum quantum number, ℓ , of an electron in a p sublevel has a value of 2.
 - Three electrons in a p sublevel will occupy separate orbitals, so one will be positive (+1), one will be neutral (0), and one will be negative (−1).
 - Two electrons in the same orbital must have the same spin.
141. Antimatter is composed of antiparticles in the same way that normal matter is composed of particles. For every subatomic particle there exists an antiparticle with the same mass but opposite charge. The antielectron (or positron) has a positive charge, and the antiproton has a negative charge. In 1995 the European Organization for Nuclear Research (commonly known as CERN) announced that it had successfully created nine antihydrogen atoms using these antiparticles. Describe the composition of an antihydrogen atom. What’s in the nucleus and what’s outside the nucleus?

Building Your Knowledge

142. ● Two isotopes of hydrogen occur naturally (^1H , > 99%, and ^2H , < 1%) and two of chlorine occur naturally (^{35}Cl , 76%, and ^{37}Cl , 24%). (a) How many different masses of HCl molecules can be formed from these isotopes? (b) What is the approximate mass of each of the molecules, expressed in atomic mass units? (Use atomic weights rounded to the nearest whole number.) (c) List these HCl molecules in order of decreasing relative abundance.
143. ● CH_4 is methane. If ^1H , ^2H , ^{12}C , and ^{13}C were the only isotopes present in a given sample of methane, show the different formulas and formula weights that might exist in that sample. (Use atomic weights rounded to the nearest whole number.)
144. Sodium is easily identified in a solution by its strong emission at $\lambda = 589 \text{ nm}$. According to Einstein’s equation, $E = mc^2$ (where m is mass), this amount of energy can be converted into mass. What is the mass equivalent of one photon emitted by an excited sodium atom?
($1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$)
145. A student was asked to calculate the wavelength and frequency of light emitted for an electron in an excited state H atom making the following transitions: (a) $n = 6 \rightarrow n = 2$, and (b) $n = 6 \rightarrow n = 3$. She was asked to determine whether she would be able to visually detect either of these electron transitions. Are her responses below correct? If not, make the necessary corrections.
- $1/\lambda = (1.097 \times 10^7/\text{m})(1/2^2 - 1/6^2) = 2.44 \times 10^6/\text{m}; \lambda = 244 \text{ nm}$
 - $1/\lambda = (1.907 \times 10^7/\text{m})(1/3^2 - 1/6^2) = 9.14 \times 10^5/\text{m}; \lambda = 1090 \text{ nm}$
- She concluded that she couldn’t see either of the transitions because neither is in the visible region of the spectrum.
146. When compounds of barium are heated in a flame, green light of wavelength 554 nm is emitted. How much energy is lost when one mole of barium atoms each emit one photon of this wavelength?



147. A 60-watt incandescent light bulb consumes energy at the rate of $60\text{ J} \cdot \text{s}^{-1}$. Much of the light is emitted in the infrared region, and less than 5% of the energy appears as visible light. Calculate the number of visible photons emitted per second. Make the simplifying assumptions that 5.0% of the light is visible and that all visible light has a wavelength of 550 nm (yellow-green).



Charles D. Winters
An incandescent light bulb

148. Classical music radio station KMFA in Austin broadcasts at a frequency of 89.5 MHz. What is the wavelength of its signal in meters?
149. (a) How many electrons are in 25.0 g of copper? (b) How many electrons are in one mole of nitrogen molecules?
150. (a) How many electrons are in one mole of nitrogen molecules? (b) How many electrons are in 30.0 g of water?

Beyond the Textbook

NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.*

151. At www.chemsoc.org/viselements, www.webelements.com, or another suitable website, locate information on scandium, vanadium, chromium, and copper that will assist you in answering the following questions.
- Which of the four elements listed was first isolated in a laboratory in Mexico?
 - Which was discovered first?
 - Which of the four elements are (is) not essential in our diet?
 - Which has only two known nonzero oxidation states?
152. Use an internet search engine (such as <http://www.google.com>) to locate a table of isotopes found in naturally occurring samples of nickel. From these data, calculate the atomic mass of nickel. How does your answer compare to the value found on the periodic table? How do the values you found compare to those in Exercise 31?
153. Use an internet search engine (such as <http://www.google.com>) to locate a table of isotopes found in naturally occurring samples of chromium. How many neutrons are present in an atom of each stable isotope of chromium? How does the data you found compare to that in Exercise 38?
154. Use an internet search engine (such as <http://www.google.com>) to locate a biography of Sir Isaac Newton. How old was he when he entered college? How old was he when he died?
155. Go to <http://numeriana.com/answer/humor.htm#units>. (a) Locate the value for microcentury expressed in minutes. (b) Locate the so-called “New Scientific Units” and give your favorite one.

Chemical Periodicity

5



The reaction of H_2O and Li (*left*) to produce LiOH and $\text{H}_2(\text{g})$ is much slower than the analogous reaction between H_2O and Na (*right*). The higher reactivity of sodium relative to lithium is one of the many predictions and trends from chemical periodicity discussed in this chapter.

Charles D. Winters

OUTLINE

5-1 More About the Periodic Table

Periodic Properties of the Elements

- 5-2 Atomic Radii
- 5-3 Ionization Energy
- 5-4 Electron Affinity
- 5-5 Ionic Radii
- 5-6 Electronegativity
- 5-7 Oxidation States

Chemical Reactions and Periodicity

- 5-8 Hydrogen and the Hydrides
 - Hydrogen
 - Reactions of Hydrogen and the Hydrides
- 5-9 Oxygen and the Oxides
 - Oxygen and Ozone
 - Reactions of Oxygen and the Oxides
 - Combustion Reactions
 - Combustion of Fossil Fuels and Air Pollution

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Understand and effectively use the periodic table
- ▶ Discuss chemical periodicity of the following physical properties:
 - Atomic radii
 - Ionization energy
 - Electron affinity
 - Ionic radii
 - Electronegativity
 - Oxidation state
- ▶ Assign oxidation states to elements when they are free, in compounds, or ions
- ▶ Describe chemical periodicity in the reactions of
 - Hydrogen
 - Oxygen
- ▶ Describe chemical periodicity in the compounds of
 - Hydrogen
 - Oxygen

5-1 More About the Periodic Table

In Chapter 4 we described the development of the periodic table, some terminology for it, and its guiding principle, the **periodic law**.

The properties of the elements are periodic functions of their atomic numbers.

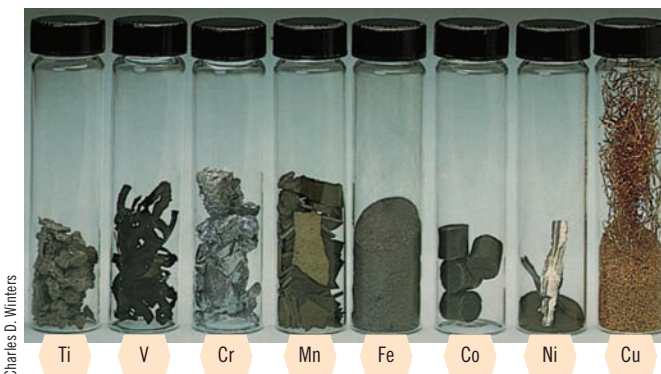
In Chapter 4 we also described electron configurations of the elements. In the long form of the periodic table, elements are arranged in blocks based on the kinds of atomic orbitals being filled. (Please review Table 4-9 and Figure 4-32 carefully.) We saw that electron configurations of all elements in the A groups can be predicted from their positions in the periodic table. We also noted, however, that some irregularities occur within the B groups.

Now we can classify the elements according to their electron configurations, which is a very useful system.

Noble Gases. For many years the Group 8A elements—the noble gases—were called inert gases because no chemical reactions were known for them. We now know that the heavier members do form compounds, mostly with fluorine and oxygen. Except for helium, each of these elements has eight electrons in its outermost occupied shell. Their outer shell may be represented as having the electron configuration $\dots ns^2np^6$.

Representative Elements. The A group elements in the periodic table are called representative elements. Their “last” electron is assigned to an outer shell s or p orbital. These elements show distinct and fairly regular variations in their properties with changes in atomic number.

- ▶ The properties of elements are correlated with their positions in the periodic table. Chemists use the periodic table as an invaluable guide in their search for new, useful materials.



Some transition metals (left to right): Ti, V, Cr, Mn, Fe, Co, Ni, Cu.

Unless otherwise noted, all content on this page is © Cengage Learning.

The Periodic Table

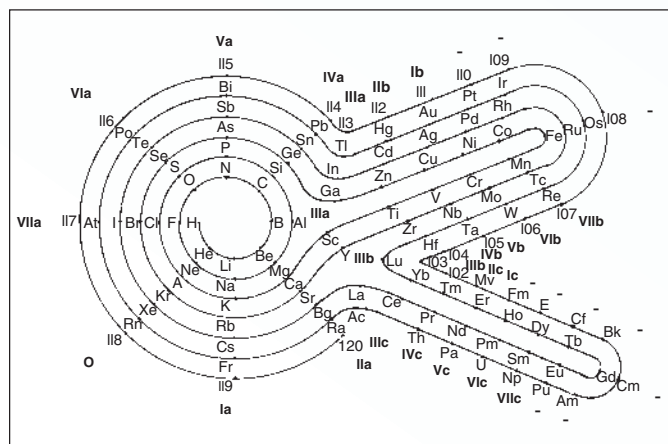
The periodic table is one of the first things a student of chemistry encounters. It appears invariably in textbooks, in lecture halls, and in laboratories. Scientists consider it an indispensable reference. And yet, less than 150 years ago, the idea of arranging the elements by atomic weight or number was considered absurd. At an 1866 meeting of the Chemical Society at Burlington House, England, J. A. R. Newlands (1837–1898) presented a theory he called the law of octaves. It stated that when the known elements were listed by increasing atomic weights, those that were eight places apart would be similar, much like notes on a piano keyboard. His colleagues' reactions are probably summed up best by the remark of a Professor Foster: "Have you thought of arranging the elements according to their initial letters? Maybe some better connections would come to light that way."

It is not surprising that poor Newlands was not taken seriously. In the 1860s, little information was available to illustrate relationships among the elements. Only 62 of them had been distinguished from more complex substances when Mendeleev first announced his discovery of the periodic law in 1869.

Mendeleev's discovery was the result of many years of hard work. He gathered information on the elements from all corners of the earth—by corresponding with colleagues, studying books and papers, and redoing experiments to confirm data. He put the statistics of each element on a small card and pinned the cards to his laboratory wall, where he arranged and rearranged them many times until he was sure that they were in the right order. One especially farsighted feature of Mendeleev's accomplishment was his realization that some elements were missing from the table. He predicted the properties of these substances (gallium, scandium, and germanium).

Since its birth in 1869, the periodic table has been discussed and revised many times. Spectroscopic and other discoveries have filled in the blanks left by Mendeleev and added a new column consisting of the noble gases. As scientists learned more about atomic structure, the basis for ordering was changed from atomic weight to atomic number. The perplexing *f*-transition elements were sorted out and given a special place, along with many of the radioactive elements created by atomic bombardment. Even the form of the table has been experimented with, resulting in everything from spiral and circular tables to exotic shapes such as the one suggested by Charles Janet (shown here).

During the past century, chemistry has become a fast-moving science in which methods and instruments are often outdated within a few



An alternative representation of the periodic table, as proposed by Charles Janet, 1928.

years. But it is doubtful that our old friend, the periodic table, will ever become obsolete. It may be modified, but it will always stand as a statement of basic relationships in chemistry and as a monument to the wisdom and insight of its creator, Dmitri Mendeleev.



The Alchemist in Search of the Philosophers' Stone Discovers Phosphorus, by Joseph Wright (1771).

The Discovery of Phosphorus

Technology and its impact on society have always been intriguing subjects for artists. This was particularly true during the Industrial Revolution, when chemistry was on the verge of transforming itself from alchemical "magic" into a scientific discipline. It is easy to see how the scientist, toiling away in a laboratory full of strange equipment and trying to make sense of the natural world, held a certain heroic appeal to artists.

One of the more romantic accounts of chemical activity during that period is *The Alchemist in Search of the Philosophers' Stone Discovers Phosphorus* (1771) by the English painter Joseph Wright of Derby (1734–1797). In Wright's depiction, a stately, bearded alchemist has just isolated a new element by distillation. As the substance collects in the flask it begins to glow in the dark, illuminating the laboratory with an eerie white light and bringing the imaginary scientist to his knees in wonder. The element phosphorus was in fact named for this property—*phosphorescence*—with both words deriving from the Greek *phosphoros*, or "giving light."

The actual discovery of elemental phosphorus was probably not quite as dramatic as Joseph Wright envisioned. It was first isolated from urine by the German chemist Henning Brand in 1669, by a much more laborious process than the one represented by the tidy distillation apparatus in Wright's painting. The first step of the preparation, as described in a 1726 treatise entitled "Phosphoros Elementalis," involved steeping 50 or 60 pails of urine in tubs for two weeks "... till it putrify and breed Worms"—hardly a fitting subject for 18th-century artwork!

Expecting a bigger reward later, Brand gave two scientific contemporaries the recipe for phosphorus in exchange for some small gifts. However, one man instead claimed the discovery for himself after repeating Brand's work in his own laboratory. Through the other, Brand did receive a contract with the Duke of Hanover for the preparation of phosphorus; however, he was dissatisfied with his pay, and it was only after writing a number of complaint letters (and enlisting his wife to do the same) that he finally received what he felt was fair compensation for his discovery.

LISA SAUNDERS BAUGH

Unless otherwise noted, all content on this page is © Cengage Learning.

d-Transition Elements. Elements in the B groups in the periodic table are known as the *d*-transition elements or, more simply, as transition elements or transition metals. The elements of the four transition series are all metals and are characterized by electrons filling the *d* orbitals. Stated differently, the *d*-transition elements contain electrons in both the *ns* and $(n - 1)d$ orbitals, but not in the *np* orbitals. The first transition series, Sc through Zn, has electrons in the 4*s* and 3*d* orbitals, but not in the 4*p* orbitals. They are referred to as

First transition series (4 <i>s</i> and 3 <i>d</i> orbitals occupied):	$_{21}\text{Sc}$ through $_{30}\text{Zn}$
Second transition series (5 <i>s</i> and 4 <i>d</i> orbitals occupied):	$_{39}\text{Y}$ through $_{48}\text{Cd}$
Third transition series (6 <i>s</i> and 5 <i>d</i> orbitals occupied):	$_{57}\text{La}$ and $_{72}\text{Hf}$ through $_{80}\text{Hg}$
Fourth transition series (7 <i>s</i> and 6 <i>d</i> orbitals occupied):	$_{89}\text{Ac}$ and $_{104}\text{Rf}$ through element 112

f-Transition Elements. Sometimes known as **inner transition elements**, these are elements in which electrons are being added to *f* orbitals. In these elements, the second from the outermost occupied shell is building from 18 to 32 electrons. All are metals. The *f*-transition elements are located between Groups 3B and 4B in the periodic table. They are

First <i>f</i> -transition series (lanthanides, 4 <i>f</i> orbitals occupied):	$_{58}\text{Ce}$ through $_{71}\text{Lu}$
Second <i>f</i> -transition series (actinides, 5 <i>f</i> orbitals occupied):	$_{90}\text{Th}$ through $_{103}\text{Lr}$

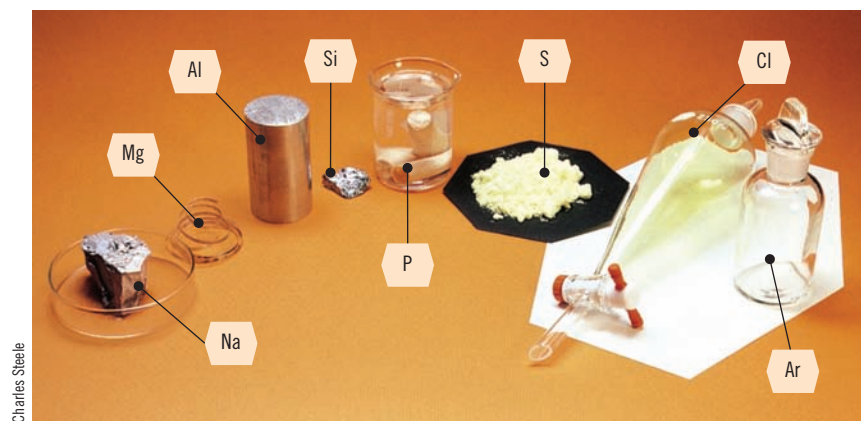
The A and B designations for groups of elements in the periodic table are somewhat arbitrary, and they may be reversed in some periodic tables. In another standard designation, the groups are numbered 1 through 18. The system used in this text is the one commonly used in the United States. Elements with the same group numbers, but with different letters, have only a few similar properties. The origin of the A and B designations is the fact that some compounds of elements with the same group numbers have similar formulas but quite different properties, for example, NaCl (1A) and AgCl (1B), MgCl₂ (2A) and ZnCl₂ (2B). As we shall see, variations in the properties of the B groups across a row are not nearly as regular and dramatic as the variations observed across a row of A group elements.

► The lanthanides are also known as the **rare earths**. They are not especially rare relative to gold and platinum, for example, but are spread out rather evenly through the earth's crust. They are also difficult to separate and purify due to their similar chemical properties. The largest concentrated deposits are in China, which has recently reduced exports, causing a dramatic increase in their prices.

► The B group elements are the transition metals.

► In any atom the *outermost* electrons are those that have the highest value of the principal quantum number, *n*.

The *outermost* or *valence* electrons have the greatest influence on the properties of elements. Adding an electron to an *s* or *p* orbital usually causes dramatic changes in the physical and chemical properties. Adding an electron to a *d* or *f* orbital typically has a smaller effect on properties.



The elements of Period 3. Properties progress (*left to right*) from solids (Na, Mg, Al, Si, P, S) to gases (Cl, Ar) and from the most metallic (Na) to the most nonmetallic (Ar). The sticks of white phosphorus are in a beaker of water because they would ignite and burn in air (O₂).

Periodic Properties of the Elements

Now we investigate the nature of periodicity. Knowledge of periodicity is valuable in understanding bonding in simple compounds. Many physical properties, such as melting points, boiling points, and atomic volumes, show periodic variations. For now, we describe the variations that are most useful in predicting chemical behavior. The changes in these properties depend on electron configurations, especially the configurations in the outermost occupied shell, and on how far away that shell is from the nucleus.

5-2 Atomic Radii

In Section 4-17 we described individual atomic orbitals in terms of probabilities of distributions of electrons over certain regions in space. Similarly, we can visualize the total electron cloud that surrounds an atomic nucleus as somewhat indefinite with no distinct edge or boundary. We cannot easily isolate a single atom and measure its diameter the way we can measure the diameter of a golf ball. For all practical purposes, the size of an individual atom cannot be uniquely defined. An indirect approach is required. The size of an atom is determined by its immediate environment, especially its interaction with surrounding atoms. By analogy, suppose we arrange some golf balls in an orderly array in a box. If we know how the balls are positioned, the number of balls, and the dimensions of the box, we can calculate the diameter of an individual ball. Application of this reasoning to solids and their densities allows us to calculate values for the atomic sizes of many elements. In other cases, we derive atomic radii from the observed distances between atoms that are combined with one another. For example, the distance between atomic centers (nuclei) in the Cl_2 molecule is measured to be $2.00 \text{ \AA}$. This suggests that the radius of *each* Cl atom is half the interatomic distance, or $1.00 \text{ \AA}$. We collect the data obtained from many such measurements to indicate the *relative* sizes of individual atoms.

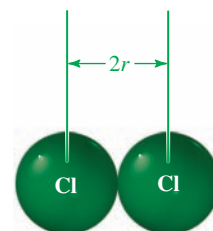
Figure 5-1 displays the relative sizes of atoms of the representative elements and the noble gases. It shows the periodicity in atomic radii.

The **effective nuclear charge**, Z_{eff} , experienced by an electron in an outer shell is less than the actual nuclear charge, Z . This is because the *attraction* of outer-shell electrons by the nucleus is partly counterbalanced by the repulsion of the outer-shell electrons by electrons in inner shells. We say that the electrons in inner shells *screen*, or *shield*, electrons in outer shells from the full effect of the nuclear charge. This concept of a **screening**, or **shielding**, **effect** helps us understand many periodic trends in atomic properties.

Consider an atom of lithium. It has two electrons in a filled shell, $1s^2$, and one electron in the $2s$ orbital, $2s^1$. The electron in the $2s$ orbital is fairly effectively screened from the nucleus by the two electrons in the filled $1s$ orbital, so the $2s$ electron does not “feel” the full $3+$ charge of the nucleus. The effective nuclear charge, Z_{eff} , experienced by the electron in the $2s$ orbital, however, is not 1 (3 minus 2) either. The electron in the outer shell of lithium has some probability of being found close to the nucleus (see Figure 4-22). We say that, to some extent, it *penetrates* the region of the $1s$ electrons; that is, the $1s$ electrons do not completely shield the outer-shell electrons from the nucleus. The electron in the $2s$ shell “feels” an effective nuclear charge a little larger than $1+$.

Sodium, element number 11, has ten electrons in inner shells, $1s^2 2s^2 2p^6$, and one electron in an outer shell, $3s^1$. The ten inner-shell electrons of the sodium atom screen (shield) the outer-shell electron from most of the $11+$ nuclear charge. Recall from Chapter 4 that the third shell ($n = 3$) is farther from the nucleus than the second shell ($n = 2$). Thus, we see why sodium atoms are larger than lithium atoms. Similar reasoning explains why potassium atoms are larger than sodium atoms and why the sizes of the elements in each column of the periodic table are related in a similar way.

► Atomic radii are often stated in **angstroms** ($1 \text{ \AA} = 10^{-10} \text{ m}$) or in the SI units **nanometers** ($1 \text{ nm} = 10^{-9} \text{ m}$) or **picometers** ($1 \text{ pm} = 10^{-12} \text{ m}$). To convert from $\text{\AA}$ to nm, move the decimal point to the left one place ($1 \text{ \AA} = 0.1 \text{ nm}$). For example, the atomic radius of Li is $1.52 \text{ \AA}$, or 0.152 nm . To convert from $\text{\AA}$ to pm, move the decimal place to the right two places, thus $1.52 \text{ \AA}$ would be 152 pm . Many European chemistry journals use pm as the standard atomic distance unit.

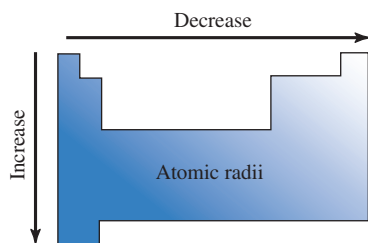


The radius of an atom, r , is taken as half of the distance between nuclei in *homonuclear* molecules such as Cl_2 .

Within a family (vertical group on the periodic table) of representative elements, atomic radii increase from top to bottom as electrons are added to shells farther from the nucleus.

1A	2A	3A	4A	5A	6A	7A	8A
H ● 0.37		Atomic radii					He ● 0.31
Li ● 1.52	Be ● 1.12	B ● 0.85	C ● 0.77	N ● 0.75	O ● 0.73	F ● 0.72	Ne ● 0.71
Na ● 1.86	Mg ● 1.60	Al ● 1.43	Si ● 1.18	P ● 1.10	S ● 1.03	Cl ● 1.00	Ar ● 0.98
K ● 2.27	Ca ● 1.97	Ga ● 1.35	Ge ● 1.22	As ● 1.20	Se ● 1.19	Br ● 1.14	Kr ● 1.12
Rb ● 2.48	Sr ● 2.15	In ● 1.67	Sn ● 1.40	Sb ● 1.40	Te ● 1.42	I ● 1.33	Xe ● 1.31
Cs ● 2.65	Ba ● 2.22	Tl ● 1.70	Pb ● 1.46	Bi ● 1.50	Po ● 1.68	At ● 1.40	Rn ● 1.41

Figure 5-1 Atomic radii of the A group (representative) elements and the noble gases, in angstroms, Å (see Section 5-2). Atomic radii *increase going down a group* because a number of electrons (8, 18, or 32 depending on the row and the presence of filled *d* and *f* orbitals) are being added to shells farther from the nucleus. Atomic radii generally *decrease from left to right within a given period* due to increasing effective nuclear charge. Hydrogen atoms are the smallest and cesium atoms are the largest naturally occurring atoms.



General trends in atomic radii of A group elements with position in the periodic table.

As we move *across* the periodic table, atoms become smaller due to increasing effective nuclear charges even though more electrons are being added. Consider the elements B ($Z = 5$, $1s^2 2s^2 2p^1$) to Ne ($Z = 10$, $1s^2 2s^2 2p^6$). In B there are two electrons in a noble gas configuration, $1s^2$, and three electrons in the second shell, $2s^2 2p^1$. The two core electrons effectively screen out most of the effect of two of the five protons in the boron nucleus. So the three electrons in the outermost orbitals only “feel” the attraction of just over three protons. Carbon ($Z = 6$, $1s^2 2s^2 2p^2$) has the same number of inner electrons ($1s^2$) to screen as boron, but the extra proton present in the nucleus provides additional attraction to pull the four outermost electrons in closer to the nucleus, making C smaller than B. This same effect continues as one moves to the right. Ne ($Z = 10$, $1s^2 2s^2 2p^6$) still has only two core electrons, but it has ten protons in the nucleus to pull the outermost electrons in even closer. Thus, even though neon has the most electrons of any element in the second row it has the smallest atomic radius. Neon is smaller, however, by only a small amount relative to fluorine because of the electron–electron repulsions that partially counter the increased effective nuclear charge.

As we move from left to right *across a period* in the periodic table, atomic radii of representative elements *decrease* as a proton is added to the nucleus and an electron is added to a particular shell.

For the transition elements, the variations are not so regular because electrons are being added to an inner shell, but the general trend of decreasing radii certainly continues as one moves across the *d*- or *f*-block metals. All transition elements have smaller radii than the preceding Group 1A and 2A elements in the same period.

Careful examination of Figure 5-1 reveals two exceptions to the decreasing atomic radius as one moves to the right in a row. The heavier main group elements Te and Po both are larger than the preceding elements. The increase in size is caused by a variety of factors, some of which are beyond the scope of a general chemistry book. One reason is the increased electron–electron repulsions caused when a fourth *p* electron is added to that shell and forced to spin-pair with one of the three unpaired *p* electrons. This leaves only two unpaired electrons available for bonding. The *s* electrons in these heavier elements are also rather “inert” and generally do not engage in any bonding interactions. Finally, the filled *d* orbitals are higher in energy due to much weaker attraction of their electrons by the nuclear charges. This causes more significant electron–electron repulsions between Te or Po atoms. These factors all work together to weaken the Te–Te and Po–Po bonds in their elemental forms, from which these radii are calculated.

EXAMPLE 5-1 Trends in Atomic Radii



Arrange the following elements in order of increasing atomic radii. Justify your order.

Cs, F, K, Cl

Plan

Both K and Cs are Group 1A metals, whereas F and Cl are halogens (7A nonmetals). Figure 5-1 shows that atomic radii increase as we descend a group, so $K < Cs$ and $F < Cl$. Atomic radii decrease from left to right.

Solution

The order of increasing atomic radii is $F < Cl < K < Cs$.

You should now work Exercise 16.

STOP & THINK

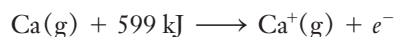
Remember the trends in atomic size—across within a row and vertically within a column.

5-3 Ionization Energy

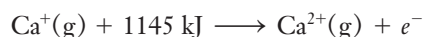
The *first ionization energy* (IE_1), also called the *first ionization potential*, is

the minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form an ion with a $1+$ charge.

For calcium, for example, the first ionization energy, IE_1 , is 599 kJ/mol:



The *second ionization energy* (IE_2) is the amount of energy required to remove the second electron. For calcium, it may be represented as



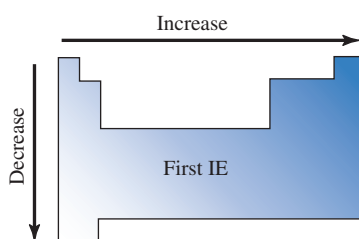
For a given element, IE_2 is *always greater than* IE_1 because it is always more difficult to remove a negatively charged electron from a positively charged ion than from the corresponding neutral atom. Table 5-1 gives first ionization energies.

Ionization energies measure how tightly electrons are bound to atoms. Ionization always requires energy to remove an electron from the attractive force of the nucleus. Low

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 5-1 First Ionization Energies (kJ/mol of atoms) of Some Elements

H 1312																	He 2372
Li 520	Be 899											B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
Na 496	Mg 738											Al 578	Si 786	P 1012	S 1000	Cl 1251	Ar 1521
K 419	Ca 599	Sc 631	Ti 658	V 650	Cr 652	Mn 717	Fe 759	Co 758	Ni 757	Cu 745	Zn 906	Ga 579	Ge 762	As 947	Se 941	Br 1140	Kr 1351
Rb 403	Sr 550	Y 617	Zr 661	Nb 664	Mo 685	Tc 702	Ru 711	Rh 720	Pd 804	Ag 731	Cd 868	In 558	Sn 709	Sb 834	Te 869	I 1008	Xe 1170
Cs 377	Ba 503	La 538	Hf 681	Ta 761	W 770	Re 760	Os 840	Ir 880	Pt 870	Au 890	Hg 1007	Tl 589	Pb 715	Bi 703	Po 812	At 890	Rn 1037

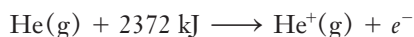


General trends in first ionization energies of A group elements with position in the periodic table. Exceptions occur at Groups 3A and 6A.

ionization energies indicate easy removal of electrons, and hence easy positive ion (cation) formation. Figure 5-2 shows a plot of first ionization energy versus atomic number for several elements.

Elements with low ionization energies (IE) easily lose electrons to form cations.

Figure 5-2 shows that each noble gas has the highest first ionization energy in its period. This should not be surprising because the noble gases are known to be very unreactive elements. It requires more energy to remove an electron from a helium atom (slightly less than 4.0×10^{-18} J/atom, or 2372 kJ/mol) than to remove one from a neutral atom of any other element.



► By Coulomb's Law, $F \propto \frac{(q^+)(q^-)}{d^2}$, the attraction for the outer shell electrons is directly proportional to the *effective* charges and inversely proportional to the *square* of the distance between the charges. Even though the effective nuclear charge increases going down a group, the greatly increased size causes a weaker net attraction for the outer electrons and thus results in a lower first ionization energy.

The Group 1A metals (Li, Na, K, Rb, Cs) have very low first ionization energies. Each of these elements has only one electron in its outermost shell ($\dots ns^1$), and they are the largest atoms in their periods. The first electron added to a shell is easily removed to form a noble gas configuration. As we move down the group, the first ionization energies become smaller. The force of attraction of the positively charged nucleus for electrons decreases as the square of the distance between them increases. So as atomic radii increase in a given group, first ionization energies decrease because the outermost electrons are farther from the nucleus.

Effective nuclear charge, Z_{eff} , increases going from left to right across a period. The increase in effective nuclear charge causes the outermost electrons to be held more tightly, making them harder to remove. The first ionization energies therefore generally *increase* from left to right across the periodic table. The reason for the trend in first ionization ener-

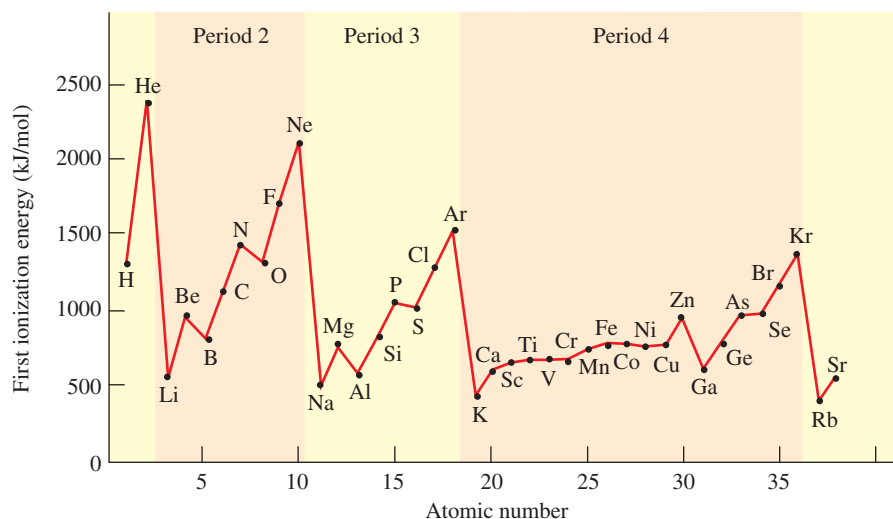


Figure 5-2 A plot of first ionization energies for the first 38 elements versus atomic number. The noble gases have very high first ionization energies, and the 1A metals have low first ionization energies. Note the similarities in the variations for the Period 2 elements, 3 through 10, to those for the Period 3 elements, 11 through 18, as well as for the later A group elements. Variations for B group elements are not nearly so pronounced as those for A group elements.

gies is the same as that used in Section 5-2 to explain trends in atomic radii. The first ionization energies of the Group 2A elements (Be, Mg, Ca, Sr, Ba) are significantly higher than those of the Group 1A elements in the same periods. This is because the Group 2A elements have higher Z_{eff} values and smaller atomic radii. Thus, their outermost electrons are held more tightly than those of the neighboring 1A metals. It is harder to remove an electron from a pair in the filled outermost s orbitals of the Group 2A elements than to remove the single electron from the half-filled outermost s orbitals of the Group 1A elements.

The first ionization energies for the Group 3A elements (B, Al, Ga, In, Tl) are exceptions to the general horizontal trends. They are *lower* than those of the 2A elements in the same periods because the 3A elements have only a single electron in their outermost p orbitals. Less energy is required to remove the first p electron than the second s electron from the outermost shell because the p orbital is at a higher energy (less stable) than an s orbital within the same shell (n value).

Going from Groups 3A to 5A, electrons are going singly into separate np orbitals, where they do not shield one another significantly. The general left-to-right increase in IE_1 for each period is interrupted by a dip between Groups 5A (N, P, As, Sb, Bi) and 6A elements (O, S, Se, Te, Po). Presumably, this behavior is because the fourth np electron in the Group 6A elements is paired with another electron in the same orbital, so it experiences greater repulsion than it would in an orbital by itself. This increased repulsion outweighs the increase in Z_{eff} , so the fourth np electron in an outer shell (Group 6A elements) is somewhat easier to remove (lower ionization energy) than is the third np electron in an outer shell (Group 5A elements). After the dip between Groups 5A and 6A, the importance of the increasing Z_{eff} outweighs the repulsion of electrons needing to be paired, and the general left-to-right increases in first ionization energies resume.

Knowledge of the relative values of ionization energies assists us in predicting whether an element is likely to form ionic or molecular (covalent) compounds. Elements with low ionization energies form ionic compounds by losing electrons to form *cations* (positively charged ions). Elements with intermediate ionization energies generally form molecular compounds by sharing electrons with other elements. Elements with very high ionization energies, such as Groups 6A and 7A, often gain electrons to form *anions* (negatively charged ions) with closed shell (noble gas) electron configurations.

One factor that favors an atom of a *representative* element forming a monatomic ion in a compound is the formation of a stable noble gas electron configuration. Energy considerations are consistent with this observation. For example, as 1 mol Li from Group 1A forms 1 mol Li^+ ions, it absorbs 520 kJ/mol. The IE_2 value is 14 times greater, 7298 kJ/mol, and is prohibitively large for the formation of Li^{2+} ions under ordinary conditions. For Li^{2+} ions to form, an electron would have to be removed from the filled first shell, which is very unlikely. The other alkali metals behave in the same way, for similar reasons.

The first two ionization energies of Be (Group 2A) are 899 and 1757 kJ/mol, but IE_3 is more than eight times larger, 14,849 kJ/mol. So Be forms Be^{2+} ions, but not Be^{3+} ions. The other alkaline earth metals—Mg, Ca, Sr, Ba, and Ra—behave in a similar way. Only the lower members of Group 3A, beginning with Al, form $3+$ ions. Bi and some d - and f -transition metals do so, too. We see that the magnitudes of successive ionization energies support the ideas of electron configurations discussed in Chapter 4.

Due to the high energy required, *simple monatomic cations with charges greater than $3+$ do not form under ordinary circumstances.*

► As one goes across a period on the periodic table, the slight breaks in the increasing ionization energies occur between Groups 2A and 3A (electrons first enter the np subshell) and again between Groups 5A and 6A (electrons are first paired in the np subshell).

► Here is one reason why trends in ionization energies are important.

► Noble gas electron configurations are stable only for ions in *compounds*. In fact, $\text{Li}^+(\text{g})$ is less stable than $\text{Li}(\text{g})$ by 520 kJ/mol.

EXAMPLE 5-2 Trends in First IEs



Arrange the following elements in order of increasing first ionization energy. Justify your order.

Na, Mg, Al, Si

Plan

The first ionization energies generally increase from left to right in the same period, but there are exceptions at Groups 3A and 6A. Al is a 3A element with only one electron in its outer p orbitals, $1s^2 2s^2 2p^6 3s^2 3p^1$, which makes the first ionization energy lower than one might normally expect.

Solution

There is a slight dip at Group 3A in the plot of first IE versus atomic number (see Figure 5-2). The order of increasing first ionization energy is $\text{Na} < \text{Al} < \text{Mg} < \text{Si}$.

You should now work Exercise 24.

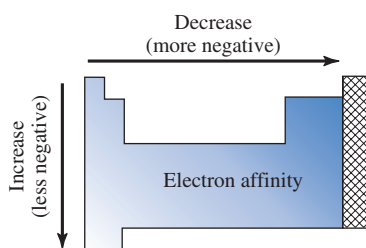
5-4 Electron Affinity

The **electron affinity (EA)** of an element may be defined as

the energy change when an electron is added to an isolated gaseous atom to form an ion with a $1-$ charge.

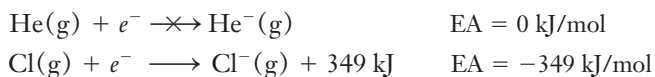
► This is consistent with thermodynamic convention.

► The value of EA for Cl can also be represented as -5.79×10^{-19} J/atom or -3.61 eV/atom. The electron volt (eV) is a unit of energy ($1 \text{ eV} = 1.6022 \times 10^{-19} \text{ J}$).



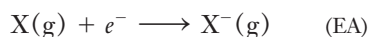
General trends in electron affinities of A group elements with position in the periodic table. There are many exceptions.

The convention is to assign a negative value when energy is released and a positive value when energy is absorbed. Most elements have no affinity for an additional electron and thus have an electron affinity equal to zero. We can represent the electron affinities of helium and chlorine as

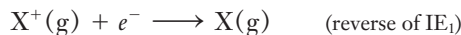


The first equation tells us that helium will not add an electron. The second equation tells us that when one mole of gaseous chlorine atoms gain one electron each to form gaseous chloride ions, 349 kJ of energy is *released (exothermic)*. Figure 5-3 shows a plot of electron affinity versus atomic number for several elements.

Electron affinity involves the *addition* of an electron to a neutral gaseous atom. The process by which a neutral atom X gains an electron



is *not* the reverse of the ionization process



The first process begins with a neutral atom, whereas the second begins with a positive ion. Thus, IE_1 and EA are *not* simply equal in value with the signs reversed. We see from Figure 5-3 that electron affinities generally become more negative from left to right across

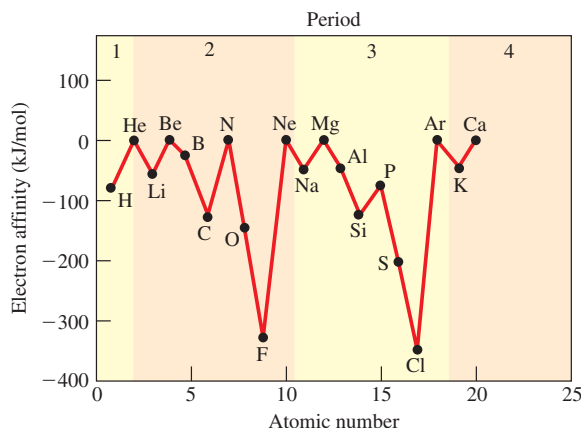


Figure 5-3 A plot of electron affinity versus atomic number for the first 20 elements. The *general* horizontal trend is that electron affinities become more negative (more energy is released as an extra electron is added) from Group 1A through Group 7A for a given period. Exceptions occur at the 2A and 5A elements.

a row in the periodic table (excluding the noble gases). This means that most representative elements in Groups 1A to 7A show a greater attraction for an extra electron from left to right. Halogen atoms, which have the outer electron configuration ns^2np^5 , have the most negative electron affinities. They form stable anions with noble gas configurations, . . . ns^2np^6 , by gaining one electron.

Elements with very negative electron affinities gain electrons easily to form negative ions (anions).

“Electron affinity” is a precise and quantitative term, like “ionization energy,” but it is difficult to measure. Table 5-2 shows electron affinities for several elements.

For many reasons, the variations in electron affinities are not regular across a period. The general trend is: the electron affinities of the elements become more negative from left to right in each period. Noteworthy exceptions are the elements of Groups 2A and 5A, which have less negative values than the trends suggest (see Figure 5-3). It is very difficult to add an electron to a 2A metal atom because its outer s subshell is filled. The values for the 5A elements are slightly less negative than expected because they apply to the addition of an electron to a half-filled set of np orbitals ($ns^2np^3 \rightarrow ns^2np^4$), which requires pairing. The resulting repulsion overcomes the increased attractive force of the nucleus.

► This reasoning is similar to that used to explain the low IE_1 values for Group 6A elements.

EXAMPLE 5-3 Trends in EAs



Arrange the following elements from most negative to least negative electron affinity.

K, Br, Cs, Cl

Plan

Electron affinity values generally become more negative from left to right across a period, with major exceptions at Groups 2A (Be) and 5A (N). They generally become more negative from bottom to top.

Solution

The order of electron affinities from most negative to least negative is

(most negative EA) Cl < Br < K < Cs (least negative EA)

This means that Cl most readily forms a $1-$ ion, while Cs is least able to do so.

You should now work Exercises 30 and 31.

► In fact, K and Cs readily form $1+$ cations.

Table 5-2 Electron Affinity Values (kJ/mol) of Some Elements*

1	H -73								He 0	
2	Li -60	Be (~0)		B -29	C -122	N 0	O -141	F -328	Ne 0	
3	Na -53	Mg (~0)		Al -43	Si -134	P -72	S -200	Cl -349	Ar 0	
4	K -48	Ca (~0)	✓	Cu -118	Ga -29	Ge -119	As -78	Se -195	Br -324	Kr 0
5	Rb -47	Sr (~0)	✓	Ag -125	In -29	Sn -107	Sb -101	Te -190	I -295	Xe 0
6	Cs -45	Ba (~0)	✓	Au -282	Tl -19	Pb -35	Bi -91			

*Estimated values are in parentheses.

Energy is always required to bring a negative charge (electron) closer to another negative charge (anion). So the addition of a second electron to a $1-$ anion to form an ion with a $2-$ charge is always endothermic. Thus, electron affinities of *anions* are always positive.

Unless otherwise noted, all content on this page is © Cengage Learning.

5-5 Ionic Radii

► The nuclear charge remains constant when the ion is formed.

Many elements on the left side of the periodic table react with other elements by *losing* electrons to form positively charged ions. Each of the Group 1A elements (Li, Na, K, Rb, Cs) has only one electron in its outermost shell (electron configuration . . . ns^1). These elements react with other elements by losing one electron to form the ions Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ , thus attaining noble gas configurations. A neutral lithium atom, Li, contains three protons in its nucleus and three electrons, with its outermost electron in the $2s$ orbital. A lithium ion, Li^+ , however, contains three protons in its nucleus but only two electrons, both in the $1s$ orbital. So a Li^+ ion is much smaller than a neutral Li atom (Figure 5-4). Likewise, a sodium ion, Na^+ , is considerably smaller than a sodium atom, Na. The relative sizes of atoms and common ions of some representative elements are shown in Figure 5-4.

Isoelectronic species have the same number of electrons. The radius of the Li^+ ion is $0.90 \text{ \AA}$, whereas the radius of the Be^{2+} ion is only $0.59 \text{ \AA}$. This is what we should expect. A beryllium ion, Be^{2+} , is formed when a beryllium atom, Be, loses both of its $2s$ electrons, while the $4+$ nuclear charge remains constant. We expect the $4+$ nuclear charge in Be^{2+} to attract the remaining two electrons quite strongly. Comparison of the ionic radii of the 2A elements with their atomic radii indicates the validity of our reasoning. We see that the ions formed by the Group 2A elements (Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) are significantly smaller than the *isoelectronic* ions formed by the Group 1A elements in the same period. Similar reasoning indicates that the ions of the Group 3A metals (Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+}) should be even smaller than the ions of Group 1A and Group 2A elements in the same periods.

Now consider the Group 7A elements (F, Cl, Br, I). These have the outermost electron configuration . . . ns^2np^5 . These elements can completely fill their outermost p orbitals by *gaining* one electron to attain noble gas configurations. Thus, when a fluorine atom (with seven electrons in its outer shell) gains one electron, it becomes a fluoride ion, F^- , with eight electrons in its outer shell. These eight electrons repel one another more strongly than the original seven, so the electron cloud expands. The F^- ion is, therefore, much larger than the

Comparison of Atomic and Ionic Radii

1A	2A	3A	5A	6A	7A
Li 1.52  Li ⁺ 0.90	Be 1.12  Be ²⁺ 0.59		N 0.75  N ³⁻ 1.71	O 0.73  O ²⁻ 1.26	F 0.72  F ⁻ 1.19
Na 1.86  Na ⁺ 1.16	Mg 1.60  Mg ²⁺ 0.85	Al 1.43  Al ³⁺ 0.68		S 1.03  S ²⁻ 1.70	Cl 1.00  Cl ⁻ 1.67
K 2.27  K ⁺ 1.52	Ca 1.97  Ca ²⁺ 1.14	Ga 1.35  Ga ³⁺ 0.76		Se 1.19  Se ²⁻ 1.84	Br 1.14  Br ⁻ 1.82
Rb 2.48  Rb ⁺ 1.66	Sr 2.15  Sr ²⁺ 1.32	In 1.67  In ³⁺ 0.94		Te 1.42  Te ²⁻ 2.07	I 1.33  I ⁻ 2.06
Cs 2.65  Cs ⁺ 1.81	Ba 2.22  Ba ²⁺ 1.49	Tl 1.70  Tl ³⁺ 1.03			

Figure 5-4 Sizes of ions of the A group representative elements, in angstroms ($\text{\AA}$), compared to the neutral covalent atoms (green). Positive ions (cations, blue) are always smaller than the neutral atoms from which they are formed. Negative ions (anions, red) are always larger than the neutral atoms from which they are formed.

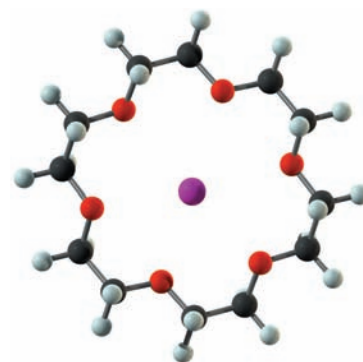
neutral F atom (see Figure 5-4). Similar reasoning indicates that a chloride ion, Cl^- , should be larger than a neutral chlorine atom, Cl. Observed ionic radii verify these predictions.

Comparing the sizes of an oxygen atom (Group 6A) and an oxide ion, O^{2-} , again we find that the negatively charged ion is larger than the neutral atom. The oxide ion is also larger than the isoelectronic fluoride ion because the oxide ion contains ten electrons held by a nuclear charge of only $8+$, whereas the fluoride ion has ten electrons held by a nuclear charge of $9+$. Comparison of radii is not a simple issue when we try to compare atoms, positive and negative ions, and ions with varying charge. Sometimes we compare atoms to their ions, atoms or ions that are vertically positioned on the periodic table, or isoelectronic species. The following guidelines are often considered.

1. Simple positively charged ions (cations) are always smaller than the neutral atoms from which they are formed.
2. Simple negatively charged ions (anions) are always larger than the neutral atoms from which they are formed.
3. Both cation and anion sizes increase going down a group.
4. Within an isoelectronic series, radii decrease with increasing atomic number because of increasing nuclear charge.

An isoelectronic series of ions

	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
Ionic radius (Å)	1.71	1.26	1.19	1.16	0.85	0.68
No. of electrons	10	10	10	10	10	10
Nuclear charge	$7+$	$8+$	$9+$	$11+$	$12+$	$13+$



Large ring compounds can selectively trap ions based on the ability of various ions to fit within a cavity in the large compound. This ball-and-stick model is an example of this with a sodium cation, Na^+ , in the middle (magenta atom). The partial negative charges on the oxygen atoms (red) attract and help hold the Na^+ within the ring. This results in selectivity such as occurs in transport across membranes in biological systems.

EXAMPLE 5-4 Trends in Ionic Radii



Arrange the following ions in order of increasing ionic radii: (a) Ca^{2+} , K^+ , Al^{3+} ; (b) Se^{2-} , Br^- , Te^{2-} .

Plan

Some of the ions are isoelectronic, so we can compare their sizes on the basis of nuclear charges. Other comparisons can be made based on the outermost occupied shell (highest value of n).

Solution

- (a) Ca^{2+} and K^+ are isoelectronic (18 electrons each) with an outer-shell electron configuration of $3s^23p^6$. Because Ca^{2+} has a higher nuclear charge ($20+$) than K^+ ($19+$), Ca^{2+} holds its 18 electrons more tightly, and Ca^{2+} is smaller than K^+ . Al^{3+} has electrons only in the second main shell (outer-shell electron configuration of $2s^22p^6$), so it is smaller than either of the other two ions.

$$\text{Al}^{3+} < \text{Ca}^{2+} < \text{K}^+$$

- (b) Br^- and Se^{2-} are isoelectronic (36 electrons each) with an outer-shell electron configuration of $4s^24p^6$. Because Br^- has a higher nuclear charge ($35+$) than Se^{2-} ($34+$), Br^- holds its 36 electrons more tightly, and Br^- is smaller than Se^{2-} . Te^{2-} has electrons in the fifth main shell (outer configuration of $5s^25p^6$), so it is larger than either of the other two ions.

$$\text{Br}^- < \text{Se}^{2-} < \text{Te}^{2-}$$

You should now work Exercises 36 and 38.

STOP & THINK

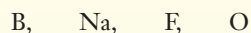
Isoelectronic species have the same number of electrons. Comparing such species, the higher the nuclear charge, the smaller the radius.

has four outermost electrons, readily loses all four to form Ti^{4+} cations. Nickel, on the other hand, has 10 outermost electrons, but rarely loses more than two of these. In general, both ionization energies and electronegativities are low for elements at the lower left of the periodic table and high for those at the upper right.

EXAMPLE 5-5 Trends in ENs



Arrange the following elements in order of increasing electronegativity.



Plan

Electronegativities increase from left to right across a period and decrease from top to bottom within a group.

Solution

The order of increasing electronegativity is $\text{Na} < \text{B} < \text{O} < \text{F}$.

You should now work Exercise 42.

Although the electronegativity scale is somewhat arbitrary, we can use it with reasonable confidence to make predictions about bonding. Two elements with quite different electronegativities (a metal and a nonmetal) tend to react with each other to form ionic compounds. The less electronegative element gives up its electron(s) to the more electronegative element. Two nonmetals with similar electronegativities tend to form covalent bonds with each other. That is, they share their electrons. In this sharing, the more electronegative element attains a greater share. This is discussed in detail in Chapters 7 and 8.

5-7 Oxidation States

Many reactions involve the transfer of electrons from one species to another. We use oxidation states to keep track of electron transfers. The systematic naming of compounds (see Sections 6-3 and 6-4) also makes use of oxidation states.

The **oxidation state**, or **oxidation number**, of an element in a simple *binary* ionic compound is the number of electrons gained or lost by an atom of that element when it forms the compound. In the case of a single-atom ion, it corresponds to the actual charge on the ion. In molecular compounds, oxidation states do not have the same significance they have in binary ionic compounds. Oxidation states, however, are very useful aids in writing formulas and in balancing equations. In molecular species, the oxidation states are assigned according to an arbitrary set of rules. The most electronegative element (farther to the right and higher up in the periodic table) is assigned a negative oxidation state, and the element farther to the left and lower down in the periodic table is assigned a positive oxidation state.

Some rules for assigning oxidation states follow. These rules are not comprehensive, but they cover most cases. In applying these rules, keep in mind two important points. First, oxidation states are always assigned on a per atom basis; second, treat the rules in order of *decreasing* importance—the first rule that applies takes precedence over any subsequent rules that seem to apply.

1. The oxidation state of the atoms in any free, uncombined element is zero. This includes polyatomic elements such as H_2 , O_2 , H_2S , P_4 , and S_8 .
2. The oxidation state of an element in a simple (monatomic) ion is equal to the charge on the ion.
3. The *sum* of the oxidation states of all atoms in a neutral compound is zero.
4. In a polyatomic ion, the *sum* of the oxidation states of the constituent atoms is equal to the charge on the ion.
5. Fluorine, the most electronegative element, has an oxidation state of -1 in all its compounds.

STOP & THINK

Electronegativity is a critical concept used throughout chemistry. You do not have to memorize the Pauling electronegativity values. Just remember that fluorine is the most electronegative element, followed by oxygen, chlorine, and nitrogen. Although Cl and N have the same Pauling electronegativity values, Cl is almost always considered by chemists to be more electronegative than N. This fluorine “corner club” defines the elements with the highest electronegativity. Cs and Fr, in the opposite corner of the periodic table, are the elements with the lowest electronegativity.

► Ionization energy (see Section 5-3) and electron affinity (see Section 5-4) are precise quantitative concepts. We find, however, that the more qualitative concept of *electronegativity* is more useful in describing chemical bonding and properties. Most chemists do not use electron affinities because it often seems to conflict with the more commonly accepted electronegativity concepts. For example, although fluorine is the most electronegative element, it has a lower electron affinity than chlorine.

► Binary means two. Binary compounds contain only two elements.

► Oxidation state and oxidation number are interchangeable terms.

► Polyatomic elements have two or more atoms per molecule.

STOP & THINK

Note that these oxidation state rules are mainly based on electronegativity trends. The most electronegative atom in a compound is assigned a negative oxidation state, while the less electronegative atom(s) lose electrons and have positive oxidation states.

► Group 5A elements have oxidation states of -3 with less electronegative elements such as H, C, or metals. When Group 5A elements are combined with more electronegative elements, positive oxidation states up to $+5$ are found.

6. Hydrogen has an oxidation state of $+1$ in compounds unless it is combined with metals, in which case it has an oxidation state of -1 . Examples of these exceptions are NaH and CaH₂.
7. Oxygen, the second most electronegative element, usually has an oxidation state of -2 in its compounds. There are just a few exceptions:
 - (a) Oxygen has an oxidation state of -1 in hydrogen peroxide, H₂O₂, and in peroxides, which contain the O₂²⁻ ion; examples are CaO₂ and Na₂O₂.
 - (b) Oxygen has an oxidation state of $-\frac{1}{2}$ in superoxides, which contain the O₂⁻ ion; examples are KO₂ and RbO₂.
 - (c) When combined with the more electronegative fluorine in OF₂, oxygen has an oxidation state of $+2$.
8. The position of the element in the periodic table helps to assign its oxidation state:
 - (a) Group 1A elements have oxidation states of $+1$ in all of their compounds.
 - (b) Group 2A elements have oxidation states of $+2$ in all of their compounds.
 - (c) Group 3A elements have oxidation states of $+3$ in all of their compounds, with a few rare exceptions.
 - (d) Group 5A elements have oxidation numbers of -3 in *binary* compounds with metals, with H, or with NH₄⁺. Exceptions are compounds with a Group 5A element combined with an element to its right in the periodic table; in this case, their oxidation states can be found by using rules 3 and 4.
 - (e) Group 6A elements below oxygen have oxidation numbers of -2 in *binary* compounds with metals, with H, or with NH₄⁺. When these elements are

Table 5-4 Common Oxidation States for Group A Elements in Compounds and Ions

Element(s)	Common Oxidation States	Examples	Other Oxidation States
H	$+1$	H ₂ O, CH ₄ , NH ₄ Cl	-1 in metal hydrides, e.g., NaH, CaH ₂
Group 1A	$+1$	KCl, NaH, RbNO ₃ , K ₂ SO ₄	None
Group 2A	$+2$	CaCl ₂ , MgH ₂ , Ba(NO ₃) ₂ , SrSO ₄	None
Group 3A	$+3$	AlCl ₃ , BF ₃ , Al(NO ₃) ₃ , GaI ₃	None in common compounds
Group 4A	$+2$ $+4$	CO, PbO, SnCl ₂ , Pb(NO ₃) ₂ CCl ₄ , SiO ₂ , SiO ₃ ²⁻ , SnCl ₄	Many others are also seen for C and Si
Group 5A	-3 in binary compounds with metals -3 in NH ₄ ⁺ , binary compounds with H	Mg ₃ N ₂ , Na ₃ P, Cs ₃ As NH ₃ , PH ₃ , AsH ₃ , NH ₄ ⁺	$+3$, e.g., NO ₂ ⁻ , PCl ₃ $+5$, e.g., NO ₃ ⁻ , PO ₄ ³⁻ , AsF ₅ , P ₄ O ₁₀
O	-2	H ₂ O, P ₄ O ₁₀ , Fe ₂ O ₃ , CaO, ClO ₃ ⁻	$+2$ in OF ₂ -1 in peroxides, e.g., H ₂ O ₂ , Na ₂ O ₂ $-\frac{1}{2}$ in superoxides, e.g., KO ₂ , RbO ₂
Group 6A (other than O)	-2 in binary compounds with metals and H -2 in binary compounds with NH ₄ ⁺	H ₂ S, CaS, Fe ₂ S ₃ , Na ₂ Se (NH ₄) ₂ S, (NH ₄) ₂ Se	$+4$ with O and the more electronegative halogens, e.g., SO ₂ , SeO ₂ , Na ₂ SO ₃ , SO ₃ ²⁻ , SF ₄ $+6$ with O and the more electronegative halogens, e.g., SO ₃ , TeO ₃ , H ₂ SO ₄ , SO ₄ ²⁻ , SF ₆
Group 7A	-1 in binary compounds with metals and H -1 in binary compounds with NH ₄ ⁺	MgF ₂ , KI, ZnCl ₂ , FeBr ₃ NH ₄ Cl, NH ₄ Br	Cl, Br, or I with O or with a more electronegative halogen $+1$, e.g., BrF, ClO ⁻ , BrO ⁻ $+3$, e.g., ICl ₃ , ClO ₂ ⁻ , BrO ₂ ⁻ $+5$, e.g., BrF ₅ , ClO ₃ ⁻ , BrO ₃ ⁻ $+7$, e.g., IF ₇ , ClO ₄ ⁻ , BrO ₄ ⁻

Unless otherwise noted, all content on this page is © Cengage Learning.

combined with oxygen or with a lighter halogen, their oxidation states can be found by using rules 3 and 4.

- (f) Group 7A elements (halogens) have oxidation states of -1 in *binary* compounds with metals, with H, with NH_4^+ , or with a heavier halogen. When these elements, except fluorine (i.e., Cl, Br, I), are combined with oxygen or with a lighter halogen, their oxidation numbers can be found by using rules 3 and 4.

Table 5-4 summarizes rules 5 through 8, with many examples.

If you use element electronegativity to guide the assignment of oxidation state, you may wonder how to proceed when two elements have the same electronegativity. Take, for example, NCl_3 , PH_3 , and CS_2 . For each of these binary compounds the elements have the same electronegativities. The periodic table is our guide, with the element that is closest to fluorine being assigned the negative oxidation state: NCl_3 (Cl = -1 , N = $+3$), PH_3 (P = -3 , H = $+1$), and CS_2 (S = -2 , C = $+4$). It is important to remember that oxidation states do not necessarily reflect reality.

EXAMPLE 5-6 Oxidation States

Determine the oxidation states of nitrogen in the following species: (a) N_2O_4 , (b) NH_3 , (c) HNO_3 , (d) NO_3^- , (e) N_2 .

Plan

We first assign oxidation states to elements that exhibit a single common oxidation number (see Table 5-4). We recall that (1) oxidation states are represented *per atom*, (2) the sum of the oxidation states in a neutral compound is zero, and (3) the sum of the oxidation states in an ion equals the charge on the ion.

Solution

- (a) The oxidation state of O is -2 . The sum of the oxidation states for all atoms in a neutral compound must be zero:

$$\begin{array}{l} \text{ox. no./atom: } \quad \textcolor{red}{x} \quad \textcolor{blue}{-2} \\ \quad \quad \quad \text{N}_2\text{O}_4 \\ \text{total ox. no.: } \quad 2x + 4(-2) = 0 \quad \text{or} \quad x = \textcolor{blue}{+4} \end{array}$$

We see that oxygen, the more electronegative element, has a negative oxidation state, while nitrogen, the less electronegative element, has the positive oxidation state.

- (b) The oxidation state of H is then $+1$:

$$\begin{array}{l} \text{ox. no./atom: } \quad \textcolor{red}{x} \quad \textcolor{blue}{+1} \\ \quad \quad \quad \text{NH}_3 \\ \text{total ox. no.: } \quad x + 3(1) = 0 \quad \text{or} \quad x = \textcolor{blue}{-3} \end{array}$$

Nitrogen is more electronegative than H, so N is in the -3 oxidation state and hydrogen is in the $+1$ state.

- (c) The oxidation state of H is $+1$ and the oxidation state of O is -2 .

$$\begin{array}{l} \text{ox. no./atom: } \quad \textcolor{blue}{+1} \quad \textcolor{red}{x} \quad \textcolor{blue}{-2} \\ \quad \quad \quad \text{HNO}_3 \\ \text{total ox. no.: } \quad 1 + x + 3(-2) = 0 \quad \text{or} \quad x = \textcolor{blue}{+5} \end{array}$$

Oxygen, the most electronegative element present, has an oxidation state of -2 , while nitrogen, being less electronegative, has a positive oxidation state.

- (d) The sum of the oxidation states for all atoms in an ion equals the charge on the ion:

$$\begin{array}{l} \text{ox. no./atom: } \quad \textcolor{red}{x} \quad \textcolor{blue}{-2} \\ \quad \quad \quad \text{NO}_3^- \\ \text{total ox. no.: } \quad x + 3(-2) = -1 \quad \text{or} \quad x = \textcolor{blue}{+5} \end{array}$$

- (e) The oxidation state of any free element is **zero**.

You should now work Exercise 46.

► Group 6A elements below oxygen have oxidation states of -2 with less electronegative elements such as H, C, or metals. When Group 6A elements are combined with more electronegative elements, positive oxidation states are found.



Aqueous solutions of some compounds that contain chromium. *Left to right:* chromium(II) chloride, CrCl_2 , is blue; chromium(III) chloride, CrCl_3 , is green; potassium chromate, K_2CrO_4 , is yellowish; potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is orangish.

► By convention, *oxidation states* are represented as $+n$ and $-n$, but ionic charges are represented as $n+$ and $n-$. We shall circle oxidation states associated with formulas and show them in colored circles indicating positive (blue), negative (red), or neutral (gray) oxidation states. Both oxidation states and ionic charges can be combined algebraically.

► Usually the element with the positive oxidation state is written first. For historic reasons, however, in compounds containing nitrogen and hydrogen, such as NH_3 , and many compounds containing carbon and hydrogen, such as CH_4 , hydrogen is written last, although it has a positive oxidation state.

Chemical Reactions and Periodicity

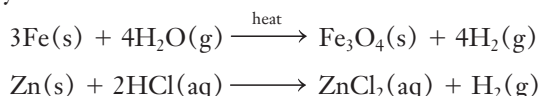
Now we will illustrate the periodicity of chemical properties by considering some reactions of hydrogen, oxygen, and their compounds. We choose to discuss hydrogen and oxygen because, of all the elements, they form the most kinds of compounds with other elements. Additionally, compounds of hydrogen and oxygen are very important in such diverse phenomena as all life processes and most corrosion.

5-8 Hydrogen and the Hydrides

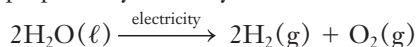
Hydrogen

► The name “hydrogen” means *water former*.

Elemental hydrogen is a colorless, odorless, tasteless diatomic gas with the lowest molecular weight and density of any known substance. Discovery of the element is attributed to the Englishman Henry Cavendish (1731–1810), who prepared it in 1766 by passing steam through a red-hot gun barrel (mostly iron) and by the reaction of acids with reactive metals. The latter is still the method commonly used for the preparation of small amounts of H_2 in the laboratory.

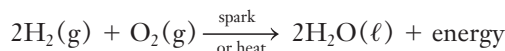


Hydrogen also can be prepared by electrolysis of water.



In the future, if it becomes economical to convert solar energy into electrical energy that can be used to electrolyze water, H_2 could become an important fuel (although the dangers of storage and transportation would have to be overcome). The *combustion* of H_2 liberates a great deal of heat. **Combustion** is the highly exothermic combination of a substance with oxygen, usually with a flame (see Section 5-9, Combustion Reactions).

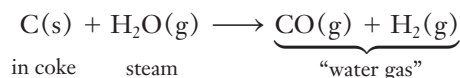
► This is the reverse of the decomposition of H_2O .



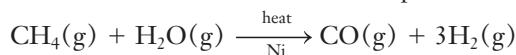
► Hydrogen is no longer used in blimps and dirigibles. It has been replaced by helium, which is slightly denser, nonflammable, and much safer.

Hydrogen is very flammable; it was responsible for the *Hindenburg* airship disaster in 1937. A spark is all it takes to initiate the **combustion reaction**, which is exothermic enough to provide the heat necessary to sustain the reaction.

Hydrogen is prepared by the “water gas reaction,” which results from the passage of steam over white-hot coke (impure carbon, a nonmetal) at 1500°C . The mixture of products commonly called “water gas” is used industrially as a fuel. Both components, CO and H_2 , undergo combustion.



Vast quantities of hydrogen are produced commercially each year by a process called *steam cracking*. Methane reacts with steam at 830°C in the presence of a nickel catalyst.



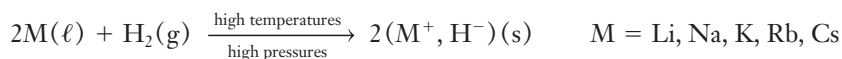
The mixture of H_2 and CO gases is also referred to as “synthesis gas.” It can be used to produce a wide variety of organic chemicals like methanol (CH_3OH) and hydrocarbon mixtures for gasoline, kerosene, and related fuels.

Reactions of Hydrogen and Hydrides

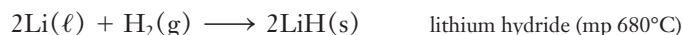
Atomic hydrogen has the $1s^1$ electron configuration. It reacts with metals and with other nonmetals to form binary compounds. When hydrogen reacts with an active metal, it gains one electron per atom to form the hydride ion, H^- ; the resulting compounds are called

ionic hydrides. In combination of hydrogen with nonmetals or metalloids, hydrogen shares electrons to form *molecular* compounds.

The ionic or molecular character of the binary compounds of hydrogen depends on the position of the other element in the periodic table (Figure 5-5). The reactions of H_2 with the *alkali* (1A) and the heavier (more active) *alkaline earth* (2A) *metals* result in solid *ionic hydrides*. The reaction with the molten (liquid) 1A metals may be represented in general terms as



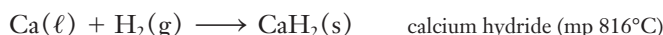
Thus, hydrogen combines with lithium to form lithium hydride and with sodium to form sodium hydride.



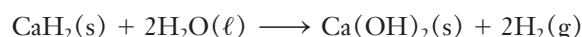
In general terms, the reactions of the heavier (more active) 2A metals may be represented as



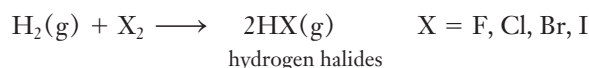
Thus, calcium combines with hydrogen to form calcium hydride:



These *ionic hydrides are all basic* because they react with water to form hydroxide ions. When water is added by drops to lithium hydride, for example, lithium hydroxide and hydrogen are produced. The reaction of calcium hydride is similar.



Hydrogen reacts with *nonmetals* to form binary *molecular compounds*. The nonmetals have higher (or equal) electronegativity relative to hydrogen, so the nonmetal takes on a negative oxidation state while hydrogen goes into the +1 oxidation state. For example, H_2 combines with the halogens to form colorless, gaseous hydrogen halides (Figure 5-6):



Specifically, hydrogen reacts with fluorine to form hydrogen fluoride and with chlorine to form hydrogen chloride:



1A	2A	3A	4A	5A	6A	7A
LiH	BeH ₂	B ₂ H ₆	CH ₄	NH ₃	H ₂ O	HF
NaH	MgH ₂	(AlH ₃) _x	SiH ₄	PH ₃	H ₂ S	HCl
KH	CaH ₂	Ga ₂ H ₆	GeH ₄	AsH ₃	H ₂ Se	HBr
RbH	SrH ₂	InH ₃	SnH ₄	SbH ₃	H ₂ Te	HI
CsH	BaH ₂	TlH	PbH ₄	BiH ₃	H ₂ Po	HAt

Figure 5-5 Common compounds of hydrogen with the representative elements. The ionic hydrides are shaded pink, molecular compounds of hydrogen are shaded green, those of intermediate character are shaded purple, and the ones in blue are acidic. The gray shaded hydrides are unstable and have not been isolated. The green and blue shaded compounds do not use hydride in their names.

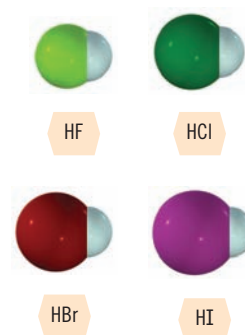
► The use of the term “hydride” does not necessarily imply the presence of the hydride ion, H^- .

► The ionic hydrides are named by naming the metal first, followed by “hydride.”

► Ionic hydrides can serve as sources of hydrogen. They must be stored in environments free of moisture and O_2 .

► We show LiOH and $Ca(OH)_2$ as solids here because not enough water is available to act as a solvent.

► The hydrogen halides are named by the word “hydrogen” followed by the stem for the halogen with an “-ide” ending.



► When the other element has similar or higher electronegativity than hydrogen, the compound with hydrogen has more molecular character. When the other element is considerably less electronegative than hydrogen, ionic hydrides containing H^- are formed (e.g., CsH).

Unless otherwise noted, all content on this page is © Cengage Learning.

► The compounds with Group 6A are named:

H₂O, hydrogen oxide (water)

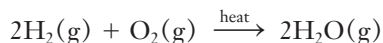
H₂S, hydrogen sulfide

H₂Se, hydrogen selenide

H₂Te, hydrogen telluride

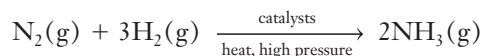
All except H₂O are very toxic.

Hydrogen combines with oxygen to form molecular compounds with a 2:1 stoichiometry:



The heavier members of the Group 6A family also combine with hydrogen to form binary compounds that are gases at room temperature. Their formulas resemble that of water.

The primary industrial use of H₂ is in the synthesis of ammonia, NH₃, by the Haber process (see Section 17-7). Most of the NH₃ is used in liquid form as a fertilizer (Figure 5-7) or to make other fertilizers, such as ammonium nitrate, NH₄NO₃, and ammonium sulfate, (NH₄)₂SO₄:



The molecular compounds of hydrogen with Groups 6A and 7A are acidic; their aqueous solutions contain hydrogen cations (H⁺). These include HF, HCl, HBr, HI, H₂S, H₂Se, and H₂Te. Acids and bases will be discussed in more detail in Chapters 6 and 10.

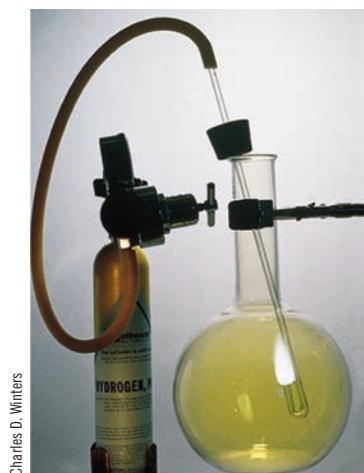


Figure 5-6 Hydrogen, H₂ burns in an atmosphere of pure chlorine, Cl₂ to produce hydrogen chloride.

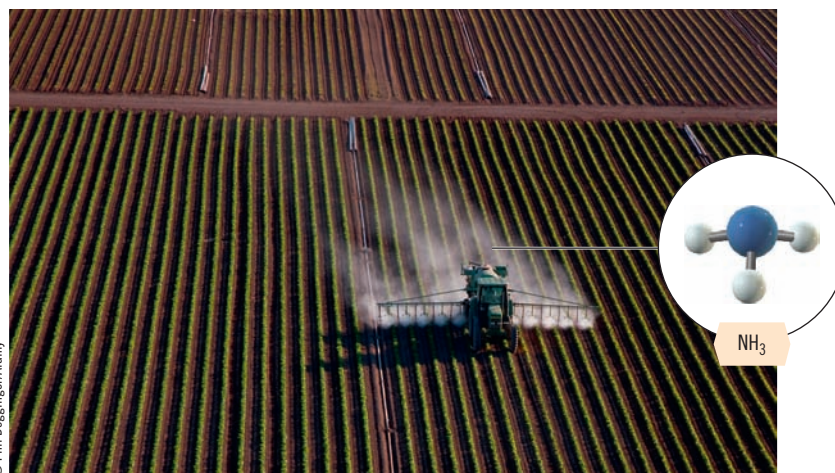
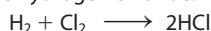
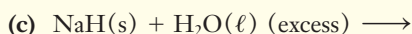
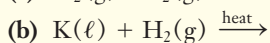
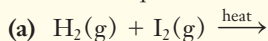


Figure 5-7 Ammonia may be applied directly to the soil as a fertilizer.

EXAMPLE 5-7 Predicting Products of Reactions

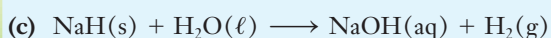
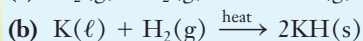
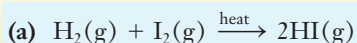
Predict the products of the reactions involving the reactants shown. Write a balanced formula unit equation for each.



Plan

- (a) Hydrogen reacts with the halogens (Group 7A) to form hydrogen halides—in this example, HI.
- (b) Hydrogen reacts with active metals to produce hydrides—in this case, KH.
- (c) Active metal hydrides react with water to produce a metal hydroxide and H₂.

Solution



► Remember that hydride ions, H[−], react with water to produce OH[−] ions and H₂(g).

EXAMPLE 5-8 Ionic and Molecular Properties

Predict the ionic or molecular character of the products in Example 5-7.

Plan

We refer to Figure 5-5, which displays the nature of binary compounds with hydrogen.

Solution

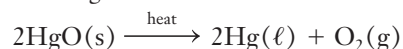
Reaction (a) is a reaction between hydrogen and another nonmetal. The product, HI, must be molecular. Reaction (b) is the reaction of hydrogen with an active Group 1A metal. Thus, KH must be ionic. The products of reaction (c) are molecular H₂(g) and the strong base, NaOH, which is ionic.

You should now work Exercises 54 and 55.

5-9 Oxygen and the Oxides

Oxygen and Ozone

Oxygen was discovered in 1774 by an English minister and scientist, Joseph Priestley (1733–1804). He observed the thermal decomposition of mercury(II) oxide, a red powder, to form liquid Hg and a colorless gas:



That part of the earth we see—land, water, and air—is approximately 50% oxygen by mass. About two-thirds of the mass of the human body is due to oxygen in H₂O. Elemental oxygen, O₂, is an odorless and colorless gas that makes up about 21% by volume of dry air. In the liquid (bp = −183°C) and solid (mp = −218°C) states, it is pale blue. Oxygen is only slightly soluble in water; only about 0.04 g dissolves in 1 L water at 25°C (0.001 M solutions). This is sufficient to sustain fish and other marine organisms. Oxygen is obtained commercially by cooling air until it liquefies and then separating N₂, O₂, Ar, and other gaseous components. The greatest single industrial use of O₂ is for oxygen enrichment in blast furnaces for the conversion of pig iron (reduced, high-carbon iron) to steel.

Oxygen also exists in a second allotropic form, called ozone, O₃. Ozone is an unstable, pale blue gas at room temperature. It is formed by passing an electrical discharge through gaseous oxygen. Its unique, pungent odor is often noticed during electrical storms and in the vicinity of electrical equipment. Not surprisingly, its density is about 1½ times that of O₂. At −112°C, it condenses to a deep blue liquid. It is a very strong oxidizing agent. As a concentrated gas or a liquid, ozone can easily decompose explosively:



Oxygen atoms, or **radicals**, are intermediates in this exothermic decomposition of O₃ to O₂. They act as strong oxidizing agents in such applications as destroying bacteria in water purification.

The ozone molecule is angular and has two oxygen–oxygen bond lengths (1.28 Å) that are identical. This is intermediate between typical single and double bond lengths between oxygen atoms.

Reactions of Oxygen and the Oxides

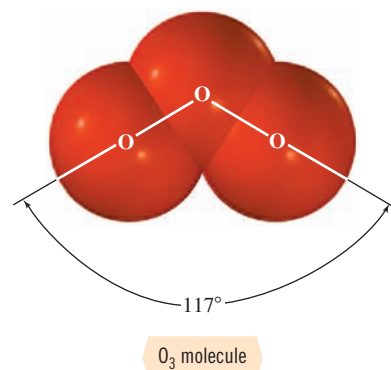
Oxygen forms oxides by direct combination with all other elements except the noble gases and noble (unreactive) metals (Au, Pd, Pt). **Oxides** are binary compounds that contain oxygen. Although such reactions are generally very exothermic, many proceed quite slowly and require heating to supply the energy necessary to break the strong bonds in O₂ mol-

► The name “oxygen” means “acid former.”

► Liquid O₂ is used as an oxidizer for rocket fuels. O₂ also is used in the health fields for oxygen-enriched air.

► Allotropes are different structural forms of the same element (see Section 2-1).

► A radical is a species containing one or more unpaired electrons; many radicals are very reactive.



Unless otherwise noted, all content on this page is © Cengage Learning.

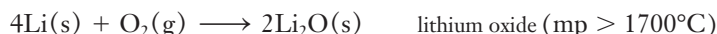
ecules. After these reactions are initiated, most release more than enough energy to be self-sustaining, and some become “red hot.”

Reactions of O₂ with Metals. Metals can combine with oxygen to form three kinds of solid ionic products called oxides, peroxides, and superoxides. You can recognize these classes of compounds as

Class	Contains Ions	Oxidation No. of Oxygen
normal oxides	O ²⁻	-2
peroxides	O ₂ ²⁻	-1
superoxides	O ₂ ⁻	- $\frac{1}{2}$

In general, metallic oxides (including peroxides and superoxides) are ionic solids.

The Group 1A metals combine with oxygen to form all three kinds of solid ionic products called oxides, peroxides, and superoxides. Lithium combines with oxygen to form lithium oxide.



By contrast, sodium reacts with an excess of oxygen to form sodium peroxide, Na₂O₂, as the major product, rather than sodium oxide, Na₂O.



Peroxides contain the O—O²⁻ ion (O₂²⁻), in which the oxidation number of each oxygen is -1, whereas **normal oxides** such as lithium oxide, Li₂O, contain oxide ions, O²⁻. The heavier members of the family (K, Rb, Cs) react with excess oxygen to form *superoxides*. These contain the **superoxide** ion, O₂⁻, in which the oxidation number of each oxygen is - $\frac{1}{2}$. The reaction with K is

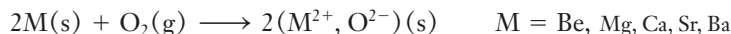


► The larger K⁺, Rb⁺, and Cs⁺ cations prefer the larger O₂⁻ and O₂²⁻ anions owing to more efficient solid-state packing, which results from better size matching of the ions.

► Beryllium reacts with oxygen only at elevated temperatures and forms only the normal oxide, BeO. The other Group 2A metals form normal oxides at moderate temperatures.

The tendency of the Group 1A metals to form oxygen-rich compounds increases going down the group. This is because cation radii increase going down the group.

The Group 2A metals react with oxygen to form normal ionic oxides, MO, but at high pressures of oxygen the heavier ones form ionic peroxides, MO₂ (Table 5-5).



For example, the equations for the reactions of calcium and oxygen are

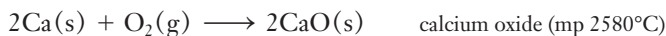


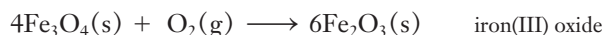
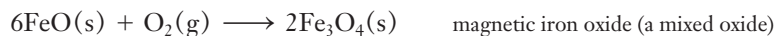
Table 5-5 Oxygen Compounds of the 1A and 2A Metals*

	1A					2A				
	Li	Na	K	Rb	Cs	Be	Mg	Ca	Sr	Ba
normal oxides	Li ₂ O	Na ₂ O	K ₂ O	Rb ₂ O	Cs ₂ O	BeO	MgO	CaO	SrO	BaO
peroxides	Li ₂ O ₂	Na ₂ O ₂	K ₂ O ₂	Rb ₂ O ₂	Cs ₂ O ₂			CaO ₂	SrO ₂	BaO ₂
superoxides		NaO ₂	KO ₂	RbO ₂	CsO ₂					

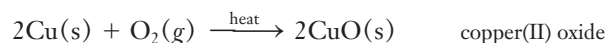
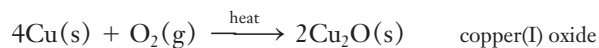
*The shaded compounds represent the principal products of the direct reaction of the metal with oxygen.

Unless otherwise noted, all content on this page is © Cengage Learning.

The other metals, with the exceptions noted previously (Au, Pd, and Pt), react with oxygen to form solid metal oxides. Many metals to the right of Group 2A show variable oxidation states, so they may form several oxides. For example, iron combines with oxygen in the following series of reactions to form three different oxides (Figure 5-8).



Copper reacts with a limited amount of oxygen to form red Cu_2O , whereas with excess oxygen it forms black CuO .



Metals that exhibit variable oxidation states react with a limited amount of oxygen to give oxides with lower oxidation states (such as FeO and Cu_2O). They react with an excess of oxygen to give oxides with higher oxidation states (such as Fe_2O_3 and CuO).



Charles D. Winters

Figure 5-8 Steel wool burns brilliantly to form iron(III) oxide, Fe_2O_3 .

Reactions of Metal Oxides with Water. Oxides of metals are called **basic anhydrides** (or **basic oxides**) because many of them combine with water to form bases with no change in oxidation state of the metal (Figure 5-9). “Anhydride” means “without water,” and in a sense, the metal oxide is a hydroxide base with the water “removed.” Metal oxides that are soluble in water react to produce the corresponding hydroxides.

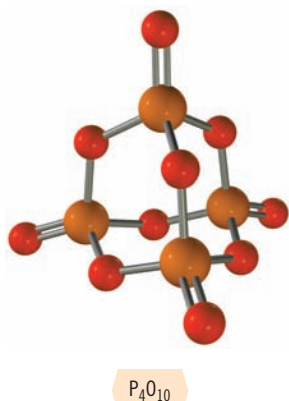
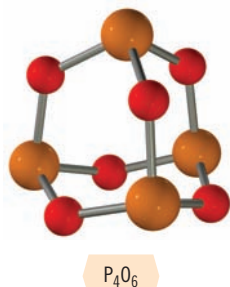
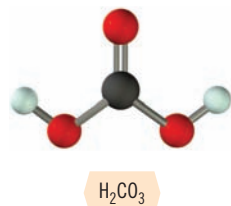
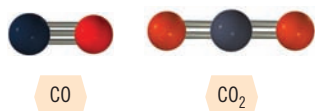
	Metal Oxide	+	Water	→	Metal Hydroxide (base)	
sodium oxide	$\text{Na}_2\text{O(s)}$	+	$\text{H}_2\text{O(l)}$	→	2NaOH(aq)	sodium hydroxide
calcium oxide	CaO(s)	+	$\text{H}_2\text{O(l)}$	→	$\text{Ca(OH)}_2\text{(aq)}$	calcium hydroxide
barium oxide	BaO(s)	+	$\text{H}_2\text{O(l)}$	→	$\text{Ba(OH)}_2\text{(aq)}$	barium hydroxide

The oxides of the Group 1A metals and the heavier Group 2A metals dissolve in water to give solutions of strong bases. Most other metal oxides are relatively insoluble in water.

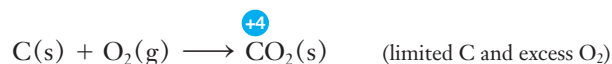
Reactions of O_2 with Nonmetals. *Oxygen combines with many nonmetals to form molecular oxides.* For example, carbon burns in oxygen to form carbon monoxide or carbon dioxide, depending on the relative amounts of carbon and oxygen.

		Increasing acidic character $\longrightarrow$					
Increasing base character $\downarrow$	1A	2A	3A	4A	5A	6A	7A
	Li_2O	BeO	B_2O_3	CO_2	N_2O_5		OF_2
	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
	K_2O	CaO	Ga_2O_3	GeO_2	As_2O_5	SeO_3	Br_2O_7
	Rb_2O	SrO	In_2O_3	SnO_2	Sb_2O_5	TeO_3	I_2O_7
	Cs_2O	BaO	Tl_2O_3	PbO_2	Bi_2O_5	PoO_3	At_2O_7

Figure 5-9 The normal oxides of the representative elements in their maximum oxidation states. Acidic oxides (acid anhydrides) are shaded blue, amphoteric oxides are shaded purple, and basic oxides (basic anhydrides) are shaded pink. An **amphoteric oxide** is one that shows some acidic and some basic properties.



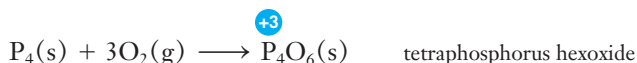
► The production of SO₃ at a reasonable rate requires the presence of a catalyst.



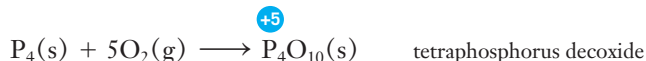
Carbon monoxide is a very poisonous gas because it forms a stronger bond with the iron atom in hemoglobin than does an oxygen molecule. Attachment of the CO molecule to the iron atom destroys the ability of hemoglobin to pick up oxygen in the lungs and carry it to the brain and muscle tissue. Carbon monoxide poisoning is particularly insidious because the gas has no odor and because the victim first becomes drowsy.

Unlike carbon monoxide, carbon dioxide is not toxic. It is one of the products of the respiratory process. It is used to make carbonated beverages, which are mostly saturated solutions of carbon dioxide in water; a small amount of the carbon dioxide combines with the water to form carbonic acid (H₂CO₃), a very weak acid.

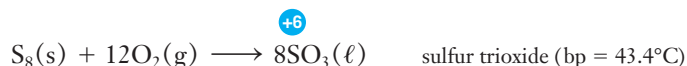
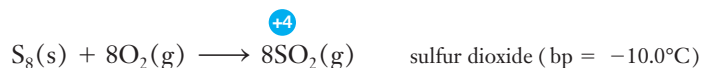
Phosphorus reacts with a limited amount of oxygen to form tetraphosphorus hexoxide, P₄O₆:



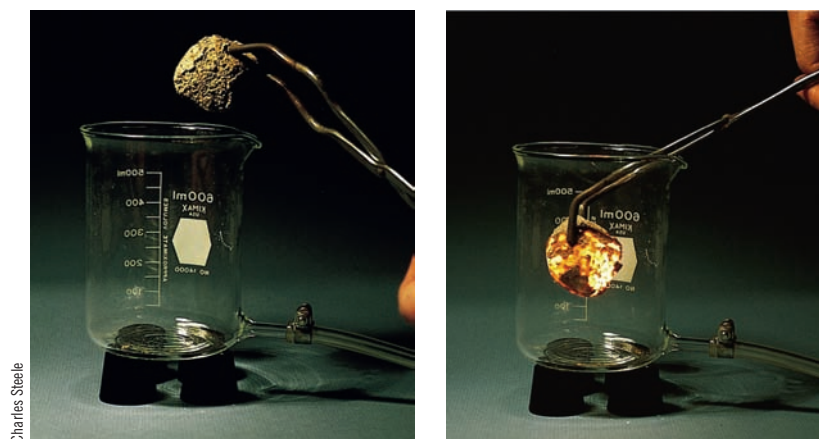
whereas reaction with an excess of oxygen gives tetraphosphorus decoxide, P₄O₁₀:



Sulfur burns in oxygen to form primarily sulfur dioxide (Figure 5-10) and only very small amounts of sulfur trioxide.



The reactions of nonmetals with a limited amount of oxygen usually give products that contain the nonmetals (other than oxygen) in lower oxidation states. Reactions with excess oxygen give products in which the nonmetals exhibit higher oxidation states. The examples we have cited are CO and CO₂, P₄O₆ and P₄O₁₀, and SO₂ and SO₃. The molecular formulas of the oxides are sometimes not easily predictable, but the *simplest* formulas are. For example, the two most common oxidation states of phosphorus in molecular compounds are +3 and +5. The simplest formulas for the corresponding phosphorus oxides therefore are P₂O₃ and P₂O₅, respectively. The molecular (true) formulas are twice these, P₄O₆ and P₄O₁₀.



Carbon burns brilliantly in pure O₂ to form CO₂.

Reactions of Nonmetal Oxides with Water. *Nonmetal oxides* are called **acid anhydrides** (or **acidic oxides**) because many of them dissolve in water to form acids *with no change in oxidation state of the nonmetal* (see Figure 5-9). Several **ternary acids** can be prepared by reaction of the appropriate nonmetal oxides with water. Ternary acids contain three elements, usually H, O, and another nonmetal.

	Nonmetal Oxide	+ Water	→ Ternary Acid	
carbon dioxide	$\overset{+4}{\text{CO}_2}(\text{g})$	$+\text{H}_2\text{O}(\ell)$	$\longrightarrow \overset{+4}{\text{H}_2\text{CO}_3}(\text{aq})$	carbonic acid
sulfur dioxide	$\overset{+4}{\text{SO}_2}(\text{g})$	$+\text{H}_2\text{O}(\ell)$	$\longrightarrow \overset{+4}{\text{H}_2\text{SO}_3}(\text{aq})$	sulfurous acid
sulfur trioxide	$\overset{+6}{\text{SO}_3}(\ell)$	$+\text{H}_2\text{O}(\ell)$	$\longrightarrow \overset{+6}{\text{H}_2\text{SO}_4}(\text{aq})$	sulfuric acid
dinitrogen pentoxide	$\overset{+5}{\text{N}_2\text{O}_5}(\text{s})$	$+\text{H}_2\text{O}(\ell)$	$\longrightarrow 2\overset{+5}{\text{HNO}_3}(\text{aq})$	nitric acid
tetraphosphorus decoxide	$\overset{+5}{\text{P}_4\text{O}_{10}}(\text{s})$	$+6\text{H}_2\text{O}(\ell)$	$\longrightarrow 4\overset{+5}{\text{H}_3\text{PO}_4}(\text{aq})$	phosphoric acid

Nearly all oxides of nonmetals and metalloids react with water to give solutions of ternary acids. The oxides of boron and silicon, which are insoluble, are two exceptions.

Reactions of Metal Oxides with Nonmetal Oxides. Another common kind of reaction of oxides is the *combination of metal oxides (basic anhydrides) with nonmetal oxides (acid anhydrides), with no change in oxidation states, to form salts*.

	Metal Oxide	+ Nonmetal Oxide	→ Salt	
calcium oxide + sulfur trioxide	$\overset{+2}{\text{CaO}}(\text{s})$	$+\overset{+6}{\text{SO}_3}(\ell)$	$\longrightarrow \overset{+2}{\text{Ca}}\overset{+6}{\text{SO}_4}(\text{s})$	calcium sulfate
magnesium oxide + carbon dioxide	$\overset{+2}{\text{MgO}}(\text{s})$	$+\overset{+4}{\text{CO}_2}(\text{g})$	$\longrightarrow \overset{+2}{\text{Mg}}\overset{+4}{\text{CO}_3}(\text{s})$	magnesium carbonate
sodium oxide + tetraphosphorus decoxide	$\overset{+1}{6\text{Na}_2\text{O}}(\text{s})$	$+\overset{+5}{\text{P}_4\text{O}_{10}}(\text{s})$	$\longrightarrow 4\overset{+1}{\text{Na}}\overset{+5}{\text{PO}_4}(\text{s})$	sodium phosphate



Figure 5-10 Sulfur burns in oxygen to form sulfur dioxide.

► More information on strong and weak acids will appear in Chapter 6.

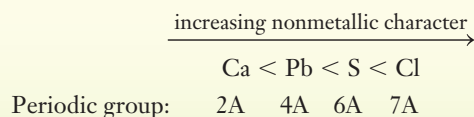
EXAMPLE 5-9 Acidic Character of Oxides



Arrange the following oxides in order of increasing molecular (acidic) character: SO_3 , Cl_2O_7 , CaO , and PbO_2 .

Plan

Molecular (acidic) character of oxides increases as nonmetallic character of the element that is combined with oxygen increases (see Figure 5-9).



Solution

Thus, the order is $\text{CaO} < \text{PbO}_2 < \text{SO}_3 < \text{Cl}_2\text{O}_7$

STOP & THINK

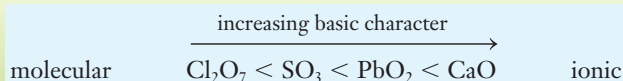
Be sure you can relate properties such as metallic character of elements and oxide character to the periodic table.

EXAMPLE 5-10 Basic Character of Oxides

Arrange the oxides in Example 6-8 in order of increasing basicity.

Plan

The greater the molecular character of an oxide, the more acidic it is. Thus, the most basic oxides have the least molecular (most ionic) character (see Figure 5-9).

Solution**EXAMPLE 5-11 Predicting Reaction Products**

Predict the products of the following pairs of reactants. Write a balanced equation for each reaction.

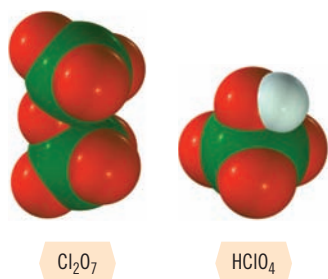
- (a) $\text{Cl}_2\text{O}_7(\ell) + \text{H}_2\text{O}(\ell) \longrightarrow$
 (b) $\text{As}_4(\text{s}) + \text{O}_2(\text{g}) (\text{excess}) \xrightarrow{\text{heat}}$
 (c) $\text{Mg}(\text{s}) + \text{O}_2(\text{g}) \xrightarrow{\text{heat}}$

Plan

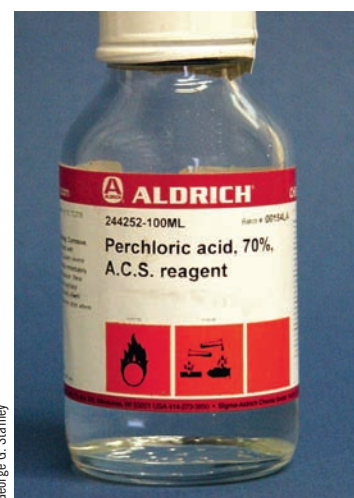
- (a) The reaction of a nonmetal oxide (acid anhydride) with water forms a ternary acid in which the nonmetal (Cl) has the same oxidation state (+7) as in the oxide. Thus, the acid is perchloric acid, HClO_4 .
 (b) Arsenic, a Group 5A metalloid, exhibits common oxidation states of +5 and $+5 - 2 = +3$. Reaction of arsenic with *excess* oxygen produces the higher-oxidation-state oxide, As_2O_5 . By analogy with the oxide of phosphorus in the +5 oxidation state, P_4O_{10} , we might write the formula as As_4O_{10} , but this oxide exists as As_2O_5 .
 (c) The reaction of a Group 2A metal with oxygen produces the normal metal oxide— MgO in this case.

Solution

- (a) $\text{Cl}_2\text{O}_7(\ell) + \text{H}_2\text{O}(\ell) \longrightarrow 2\text{HClO}_4(\text{aq})$
 (b) $\text{As}_4(\text{s}) + 5\text{O}_2(\text{g}) \xrightarrow{\text{heat}} 2\text{As}_2\text{O}_5(\text{s})$
 (c) $2\text{Mg}(\text{s}) + \text{O}_2(\text{g}) \xrightarrow{\text{heat}} 2\text{MgO}(\text{s})$

**CAUTION!**

Perchloric acid is an especially dangerous strong acid because it is also a very strong oxidizing acid. The perchlorate salts produced from its reactions with bases are prone to explosions if they are touched or disturbed when dry.



George G. Stanley

EXAMPLE 5-12 Predicting Reaction Products

Predict the products of the following pairs of reactants. Write a balanced equation for each reaction.

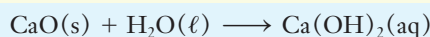
- (a) $\text{CaO(s)} + \text{H}_2\text{O(l)} \longrightarrow$
 (b) $\text{Li}_2\text{O(s)} + \text{SO}_3\text{(l)} \longrightarrow$

Plan

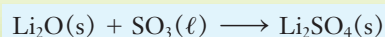
- (a) The reaction of a metal oxide with water produces the metal hydroxide.
 (b) The reaction of a metal oxide with a nonmetal oxide produces a salt containing the cation of the metal oxide and the anion of the acid for which the nonmetal oxide is the anhydride. SO_3 is the acid anhydride of sulfuric acid, H_2SO_4 .

Solution

- (a) Calcium oxide reacts with water to form calcium hydroxide.



- (b) Lithium oxide reacts with sulfur trioxide to form lithium sulfate.

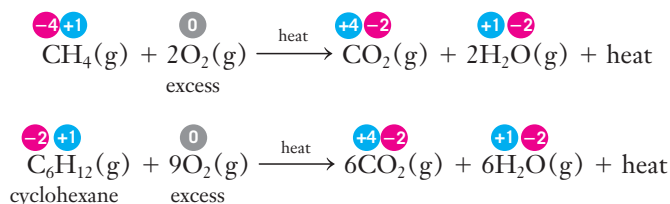


You should now work Exercises 66–69.

► CaO is called quicklime. Ca(OH)_2 is called slaked lime. Both are sometimes just called lime.

Combustion Reactions

Combustion, or burning, is an oxidation–reduction reaction in which oxygen combines rapidly with oxidizable materials in highly exothermic reactions, usually with a visible flame. The complete combustion of *hydrocarbons*, in fossil fuels for example, produces carbon dioxide and water (steam) as the major products:



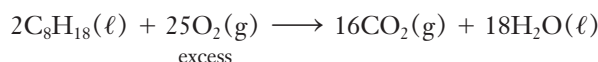
► Hydrocarbons are compounds that contain only hydrogen and carbon.

As we have seen, the origin of the term “oxidation” lies in just such reactions, in which oxygen “oxidizes” another species.

► Recall that oxidation states are indicated by numbers in colored circles (blue for positive oxidation states, red for negative oxidation states, and gray for 0).

Combustion of Fossil Fuels and Air Pollution

Fossil fuels are mixtures of variable composition that consist primarily of hydrocarbons. We burn them to use the energy that is released rather than to obtain chemical products (Figure 5-11). For example, burning octane, C_8H_{18} , in an excess of oxygen (plenty of air) produces carbon dioxide and water. There are many similar compounds in gasoline and diesel fuels.



Carbon monoxide is produced by the incomplete burning of carbon-containing compounds in a limited amount of oxygen.

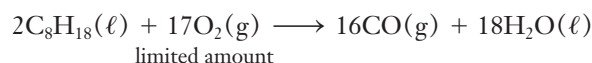
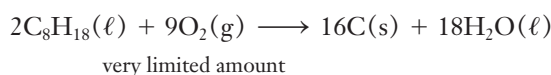


Figure 5-11 Plants such as this one burn more than 10^7 tons of coal and produce over 2×10^8 megawatt-hours of electricity each year.

► Carbon in the form of soot is one of the many kinds of *particulate matter* in polluted air.

In very limited oxygen, carbon (soot) is produced by partially burning hydrocarbons. For octane, the reaction is

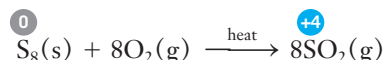


When you see blue or black smoke (carbon) coming from an internal combustion engine (or smell unburned fuel in the air), you may be quite sure that lots of toxic carbon monoxide is also being produced and released into the air.

We see that the incomplete combustion of hydrocarbons yields undesirable products—carbon monoxide and elemental carbon (soot), which pollute the air. Unfortunately, all fossil fuels—natural gas, coal, gasoline, kerosene, oil, and so on—also have undesirable nonhydrocarbon impurities that burn to produce oxides that act as additional air pollutants. At this time it is not economically feasible to remove all of these impurities from the fuels before burning them.

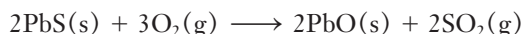
Fossil fuels result from the decay of animal and vegetable matter (Figure 5-12). All living matter contains some sulfur and nitrogen, so fossil fuels also contain sulfur and nitrogen impurities to varying degrees. Table 5-6 gives composition data for some common kinds of coal.

Combustion of sulfur produces sulfur dioxide, SO_2 , probably the single most harmful pollutant.



Large amounts of SO_2 are produced by the burning of sulfur-containing coal.

Many metals occur in nature as sulfides. The process of extracting the free (elemental) metals involves **roasting**—heating an ore in the presence of air. For many metal sulfides this produces a metal oxide and SO_2 . The metal oxides are then reduced to the free metals. Consider lead sulfide, PbS , as an example:



Sulfur dioxide is corrosive; it damages plants, structural materials, and humans. It is a nasal, throat, and lung irritant. Sulfur dioxide is slowly oxidized to sulfur trioxide, SO_3 , by oxygen in air:

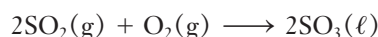


Table 5-6 Some Typical Coal Compositions in Percent (dry, ash-free)

	C	H	O	N	S
lignite	70.59	4.47	23.13	1.04	0.74
subbituminous	77.2	5.01	15.92	1.30	0.51
bituminous	80.2	5.80	7.53	1.39	5.11
anthracite	92.7	2.80	2.70	1.00	0.90

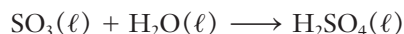
The Blue Ridge Mountain next to Palmerton, Pennsylvania, was decimated by SO_2 pollution from the zinc refinery located there. The roasting of the ZnS ore to produce ZnO (used to produce Zn metal) also made SO_2 most of which was captured to generate sulfuric acid. But cumulative SO_2 releases over many years killed most of the vegetation on the mountain next to the refinery. The refinery is now shut down, and the Environmental Protection Agency (EPA) is doing extensive remediation of the mountain with acid- and zinc-resistant plants.

Unless otherwise noted, all content on this page is © Cengage Learning.



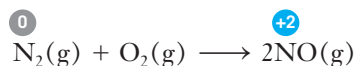
© John Bartholomew/Corbis

Sulfur trioxide readily combines with moisture in the air to form the strong, corrosive acid, sulfuric acid:

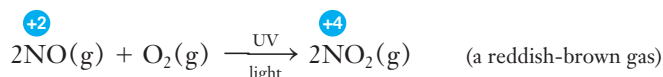


Oxides of sulfur are the main cause of acid rain.

Compounds of nitrogen are also impurities in fossil fuels; they burn to form nitric oxide, NO. Most of the nitrogen in the NO in exhaust gases from furnaces, automobiles, airplanes, and so on, however, comes from the air that is mixed with the fuel.

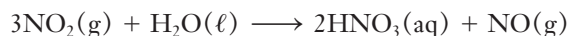


NO can be further oxidized by oxygen to nitrogen dioxide, NO₂; this reaction is enhanced in the presence of ultraviolet light from the sun.



NO₂ is responsible for the reddish-brown haze that hangs over many cities on sunny afternoons (Figure 5-13) and probably for most of the respiratory problems associated with this kind of air pollution. It can react to produce other oxides of nitrogen and other secondary pollutants.

In addition to being a pollutant itself, nitrogen dioxide reacts with water in the air to form nitric acid, another major contributor to acid rain:



► Remember that “clean air” is about 80% N₂ and 20% O₂ by mass. This reaction does *not* occur at room temperature but does occur at the high temperatures of furnaces, internal combustion engines, and jet engines.



Figure 5-13 Photochemical pollution (a brown haze) enveloping a city.

KEY TERMS

Acid anhydride A nonmetal oxide that reacts with water to form an acid.

Acidic oxide See *Acid anhydride*.

Actinides Elements 90 through 103 (after *actinium*).

Amphoteric oxide An oxide that shows some acidic and some basic properties.

Amphoterism The ability of a substance to react with both acids and bases.

Angstrom (Å) 10⁻¹⁰ meter, 10⁻¹ nm, or 100 pm.

Atomic radius The radius of an atom.

Basic anhydride A metal oxide that reacts with water to form a base.

Basic oxide See *Basic anhydride*.

Catalyst A substance that speeds up a chemical reaction without itself being consumed in the reaction.

Combustion reaction The rapid oxidation–reduction reaction of an oxidizable substance with oxygen in a highly exothermic reaction, usually with a visible flame.

d-Transition elements (metals) The B group elements in the periodic table; sometimes called simply transition elements.

Effective nuclear charge (Z_{eff}) The nuclear charge experienced by the outermost electrons of an atom; the actual nuclear charge minus the effects of shielding due to inner shell electrons.

Electron affinity (EA) The amount of energy absorbed in the process in which an electron is added to a neutral isolated gaseous atom to form a gaseous ion with a 1 – charge; has a negative value if energy is released.

Electronegativity (EN) A measure of the relative tendency of an atom to attract electrons to itself when chemically combined with another atom.

f-Transition elements (metals) Elements 58 through 71 and 90 through 103; also called inner transition elements (metals).

Inner transition elements See *f-Transition elements*.

Ionic hydride An ionic compound that contains the hydride ion, H⁻.

Ionic radius The radius of an ion.

Ionization energy The amount of energy required to remove the most loosely held electron of an isolated gaseous atom or ion.

Isoelectronic Having the same number of electrons.

Lanthanides Elements 58 through 71 (after *lanthanum*); also known as *rare earth elements*.

Noble gas configuration The stable electron configuration of a noble gas.

Noble gases Elements of periodic Group 8A; also called rare gases; formerly called inert gases.

Normal oxide A metal oxide containing the oxide ion, O²⁻ (oxygen in the –2 oxidation state).

Oxidation states (numbers) Arbitrary numbers that can be used as aids in writing formulas and balancing equations; for single-atom ions they correspond to the charge on the ion; less metallic elements are assigned negative oxidation states in compounds and ions.

Oxide A binary compound of oxygen.

Periodicity Regular periodic variations of properties of elements with atomic number and position in the periodic table.

Periodic law The properties of the elements are periodic functions of their atomic numbers.

Peroxide A compound containing oxygen in the –1 oxidation state. Metal peroxides contain the peroxide ion, O₂²⁻.

Radical A species containing one or more unpaired electrons; many radicals are very reactive.

Unless otherwise noted, all content on this page is © Cengage Learning.

20. What is the usual relationship between atomic radius and first ionization energy, other factors being equal?
21. What is the usual relationship between nuclear charge and first ionization energy, other factors being equal?
22. Going across a period on the periodic table, what is the relationship between shielding and first ionization energy?
23. Within a group on the periodic table, what is the relationship between shielding and first ionization energy?
24. Arrange the members of each of the following sets of elements in order of increasing first ionization energies: (a) the alkali metals; (b) the halogens; (c) the elements in the second period; (d) Br, F, B, Ga, Cs, and H.
25. The following series of five ionization energies pertains to an element in the second period: $IE_1 = 1.33 \times 10^{-21}$ kJ/atom; $IE_2 = 4.03 \times 10^{-21}$ kJ/atom; $IE_3 = 6.08 \times 10^{-21}$ kJ/atom; $IE_4 = 4.16 \times 10^{-20}$ kJ/atom; $IE_5 = 5.45 \times 10^{-20}$ kJ/atom. Identify the element, and explain why you selected that element.
26. What is the general relationship between the sizes of the atoms of Period 2 and their first ionization energies? Rationalize the relationship.
27. In a plot of first ionization energy versus atomic number for Periods 2 and 3, "dips" occur at the 3A and 6A elements. Account for these dips.
28. On the basis of electron configurations, would you expect a Li^{2+} ion to exist in compounds? Why or why not? How about Be^{2+} ?
29. How much energy, in kilojoules, must be absorbed by 1.25 mol of gaseous lithium atoms to convert all of them to gaseous Li^+ ions?
32. The electron affinities of the halogens are much more negative than those of the Group 6A elements. Why is this so?
33. The addition of a second electron to form an ion with a $2-$ charge is always endothermic. Why is this so?
34. Write the equation for the change described by each of the following, and write the electron configuration for each atom or ion shown: (a) the electron affinity of oxygen; (b) the electron affinity of chlorine; (c) the electron affinity of magnesium.

Ionic Radii

35. Select the smaller member of each pair. (a) N and N^{3-} ; (b) Ba and Ba^{2+} ; (c) Se and Se^{2-} ; (d) Co^{2+} and Co^{3+}
36. Arrange the members of each of the following sets of cations in order of increasing ionic radii: (a) K^+ , Ca^{2+} , Ga^{3+} ; (b) Ca^{2+} , Be^{2+} , Ba^{2+} , Mg^{2+} ; (c) Al^{3+} , Sr^{2+} , Rb^+ , K^+ ; (d) K^+ , Ca^{2+} , Rb^+ .
37. Study the radii of Cl and Cl^- in Figure 5-4. Why is one larger than the other?
38. Arrange the following sets of anions in order of increasing ionic radii: (a) Cl^- , S^{2-} , P^{3-} ; (b) O^{2-} , S^{2-} , Se^{2-} ; (c) N^{3-} , S^{2-} , Br^- , P^{3-} ; (d) Cl^- , Br^- , I^- .
39. Select the atom or ion in each pair that has the smaller radius. (a) Cs or Rb; (b) O^{2-} or O; (c) Br or As; (d) Ba or Ba^{2+} ; (e) Cl^- or Ca^{2+}
40. Most transition metals can form more than one simple positive ion. For example, iron forms both Fe^{2+} and Fe^{3+} ions, and tin forms both Sn^{2+} and Sn^{4+} ions. Which is the smaller ion of each pair, and why?

Electronegativity

41. What is electronegativity?
42. Arrange the members of each of the following sets of elements in order of increasing electronegativities: (a) Pb, C, Sn, Ge; (b) S, Na, Mg, Cl; (c) P, N, Sb, Bi; (d) Se, Ba, F, Si, Sc.
43. Which of the following statements is better? Why? (a) Magnesium has a weak attraction for electrons in a chemical bond because it has a low electronegativity. (b) The electronegativity of magnesium is low because magnesium has a weak attraction for electrons in a chemical bond.
44. Arrange the elements Na, Si, and S in order of (a) increasing atomic radius; (b) increasing first ionization energy; (c) decreasing electronegativity.
45. One element takes on only a negative oxidation number when combined with other elements. From the table of electronegativity values, determine which element this is.

Oxidation States

46. Assign oxidation states to the element specified in each group of compounds. (a) P in PCl_3 , P_2O_5 , P_4O_{10} , HPO_3 , H_3PO_3 , $POCl_3$, $H_4P_2O_7$, $Mg_3(PO_4)_2$; (b) Br in Br^- , BrO^- , BrO_2^- , BrO_3^- , BrO_4^- ; (c) Mn in MnO , MnO_2 , $Mn(OH)_2$, K_2MnO_4 , $KMnO_4$, Mn_2O_7 ; (d) O in OF_2 , Na_2O , Na_2O_2 , KO_2 .
47. Assign oxidation states to the element specified in each group of compounds. (a) N in NO , N_2O_3 , N_2O_4 , NH_4Cl ,



Charles D. Winters

Lithium

30. Arrange the following elements in order of increasing negative values of electron affinity: P, S, Cl, and Br.
31. Arrange the members of each of the following sets of elements in order of increasingly negative electron affinities: (a) the Group 1A metals; (b) the Group 4A elements; (c) the elements in the second period; (d) Li, K, C, F, and Cl.



Charles D. Winters

Some uses of Group 4A elements



Molecular Reasoning exercises



More Challenging exercises

Blue-Numbered

exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

- N_2H_4 , NH_2OH , HNO_2 , HNO_3 ; (b) C in CO , CO_2 , CH_2O , CH_4O , $\text{C}_2\text{H}_6\text{O}$, Na_2CO_3 , C_6H_6 ; (c) S in S^{2-} , SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, H_2S .
48. Assign oxidation states to the element specified in each group of ions. (a) N in N^{3-} , NO_2^- , NO_3^- , N_3^- , NH_4^+ ; (b) Cl in Cl_2 , HCl , HClO , HClO_2 , KClO_3 , Cl_2O_7 , $\text{Ca}(\text{ClO}_4)_2$, PCl_5 .
49. Assign oxidation states to the element specified in each group. (a) S in S_8 , H_2S , SO_2 , SO_3 , Na_2SO_3 , H_2SO_4 , K_2SO_4 ; (b) Cr in CrO_2^- , $\text{Cr}(\text{OH})_4^-$, CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$; (c) B in BO_2^- , BO_3^{3-} , $\text{B}_4\text{O}_7^{2-}$.

Periodic Properties

50. Compare the respective values of the first ionization energy (see Table 5-1) and electron affinity (see Table 5-2) for several elements. Which energy is greater? Why?
51. Compare the respective values of the first ionization energy (see Table 5-1) and electron affinity (see Table 5-2) for nitrogen to those for carbon and oxygen. Explain why the nitrogen values are considerably different.

Hydrogen and the Hydrides

52. Summarize the physical properties of hydrogen.
53. Write balanced equations for (a) the reaction of iron with steam, (b) the reaction of calcium with hydrochloric acid, (c) the electrolysis of water, and (d) the “water gas” reaction.
54. Write a balanced equation for the preparation of (a) an ionic hydride and (b) a binary molecular compound of hydrogen.
55. Classify the following compounds as molecular or ionic: (a) NaH ; (b) H_2S ; (c) AlH_3 ; (d) RbH ; (e) NH_3 .
56. Explain why NaH and H_2S have different degrees of ionic character.
57. Write balanced equations for the reactions with water of (a) CaH_2 , (b) AlH_3 , and (c) NaH .



Charles D. Winters

58. Name the following (pure) compounds: (a) H_2S ; (b) HCl ; (c) KH ; (d) NH_3 ; (e) H_2Se ; (f) MgH_2 ; (g) AlH_3 .
59. Write a balanced equation for the reaction of an ionic hydride with water. What products are always formed during these reactions?

Oxygen and the Oxides

60. Briefly compare and contrast the properties of oxygen with those of hydrogen.

61. Write molecular equations to show how oxygen can be prepared from (a) mercury(II) oxide, HgO ; (b) hydrogen peroxide, H_2O_2 ; and (c) potassium chlorate, KClO_3 .
62. ▲ Which of the following elements form normal oxides as the *major* products of reactions with oxygen? (a) Li; (b) Ba; (c) Rb; (d) Mg; (e) Zn (exhibits only one common oxidation state); (f) Al.
63. Oxygen has a positive oxidation number when combined with which element? Compare the electronegativity values of oxygen and that element.
64. Write balanced equations for the reactions of the following elements with a *limited* amount of oxygen: (a) C; (b) As_4 ; (c) Ge.
65. Write balanced equations for the reactions of the following elements with an *excess* of oxygen: (a) C; (b) As_4 ; (c) Ge.
66. Distinguish among normal oxides, peroxides, and superoxides. What is the oxidation state of oxygen in each case?
67. ▲ Which of the following can be classified as basic anhydrides? (a) CO_2 ; (b) Li_2O ; (c) SeO_3 ; (d) CaO ; (e) N_2O_5 .
68. Write balanced equations for the following reactions and name the products: (a) carbon dioxide, CO_2 , with water; (b) sulfur trioxide, SO_3 , with water; (c) selenium trioxide, SeO_3 , with water; (d) dinitrogen pentoxide, N_2O_5 , with water; and (e) dichlorine heptoxide, Cl_2O_7 , with water.
69. Write balanced equations for the following reactions and name the products: (a) sodium oxide, Na_2O , with water; (b) calcium oxide, CaO , with water; (c) lithium oxide, Li_2O , with water; (d) magnesium oxide, MgO , with sulfur dioxide, SO_2 ; and (e) calcium oxide, CaO , with carbon dioxide, CO_2 .
70. ▲ Identify the acid anhydrides of the following ternary acids: (a) H_2SO_4 ; (b) H_2CO_3 ; (c) H_2SO_3 ; (d) H_3PO_4 ; (e) HNO_2 .
71. Identify the basic anhydrides of the following metal hydroxides: (a) NaOH ; (b) $\text{Mg}(\text{OH})_2$; (c) $\text{Fe}(\text{OH})_2$; (d) $\text{Al}(\text{OH})_3$.

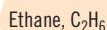
Combustion Reactions

72. ● Define combustion. Write a balanced equation for the combustion of diatomic hydrogen.
73. ● Write equations for the complete combustion of the following compounds: (a) methane, $\text{CH}_4(\text{g})$; (b) propane, $\text{C}_3\text{H}_8(\text{g})$; (c) ethanol, $\text{C}_2\text{H}_5\text{OH}(\ell)$.

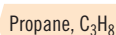


Charles D. Winters

75.  Ethane, C_2H_6 , burns in excess oxygen to form carbon dioxide and water. To illustrate this reaction, two molecules of ethane will react in the presence of nine molecules of oxygen, O_2 , to yield four molecules of carbon dioxide, six molecules of water, and two molecules of excess oxygen left unreacted.



76.  Propane, C_3H_8 , burns in excess oxygen to form carbon dioxide and water. To illustrate this reaction, a molecule of propane reacts in the presence of seven molecules of oxygen, O_2 , to yield three molecules of carbon dioxide, four molecules of water, and two molecules of excess oxygen left unreacted.



77. ▲ (a) How much SO_2 would be formed by burning 1.00 kg of bituminous coal that is 5.15% sulfur by mass? Assume that all of the sulfur is converted to SO_2 . (b) If 19.0% of the SO_2 escaped into the atmosphere and 75.0% of the escaped SO_2 were converted to H_2SO_4 , how many grams of H_2SO_4 would be produced in the atmosphere?
78. ▲ Write equations for the complete combustion of the following compounds. Assume that sulfur is converted to SO_2 and nitrogen is converted to NO . (a) $\text{C}_6\text{H}_5\text{NH}_2(\ell)$; (b) $\text{C}_2\text{H}_5\text{SH}(\ell)$; (c) $\text{C}_7\text{H}_{10}\text{NO}_2\text{S}(\ell)$.

79. Write the electron configuration for the product of the second ionization of the third largest alkaline earth metal.

80. You are given the atomic radii of 110 pm, 118 pm, 120 pm, 122 pm, and 135 pm, but do not know to which element

81. Which is larger, Na^+ or F^- ? For each of these ions, draw a representation of the shape of the highest energy occupied orbital.
82. Write the electron configurations of beryllium and magnesium. What similarities in their chemical properties can you predict on the basis of their electron configurations? Compare the sizes of their most stable ions.
83. Dolostone is often more porous than limestone. One explanation of the origin of dolostone is that it results from partial replacement of calcium by magnesium in an original limestone sediment. Is this explanation reasonable, given what you know of the ionic radii of magnesium and calcium ions?
84. On an outline of the periodic table like the one below, label the areas in which the “last” electron assigned in the electron configuration is in a filled orbital of each of the following types: $1s$, $2s$, $2p$, $3s$, $3p$, $3d$, $4s$, $4p$, $4d$, $4f$, $5s$, $5p$, $5d$, $5f$, $6s$, $6p$, $6d$, $7s$, and $7p$.

[illegible]

85. Generally, elements with very negative electron affinities gain electrons easily to form negative ions. Which group of elements tends to form anions most easily?
86. Identify all the elements that have an electronegativity of 3.0 or greater. Where are they located on the periodic table? Identify all the elements that have an electronegativity of 1.0 or less. Except for Yb, where are they located on the periodic table?
87. Figure 5-9 includes the formulas of the normal oxides of the representative elements in their maximum oxidation states. Use these formulas to determine the oxidation state of each element, assuming an oxidation state of -2 for oxygen. What is the oxidation state of every element in Groups 1A, 2A, 3A, 4A, 5A, and 6A? What is the oxidation state of most elements in Group 7A? Which element is the exception?

88. Hydrogen can be obtained from water by electrolysis. Hydrogen may someday be an important replacement for current fuels. Describe some of the problems that you would predict if hydrogen were used in today's motor vehicles.

89. The only chemically stable ion of rubidium is Rb^+ . The most stable monoatomic ion of bromine is Br^- . Krypton (Kr) is among the least reactive of all elements. Compare the electron configurations of Rb^+ , Br^- , and Kr. Then predict the most stable monatomic ions of strontium (Sr) and selenium (Se).
90. The first ionization energy of potassium, K, is 419 kJ/mol. What is the minimum frequency of light required to ionize gaseous potassium atoms?
91. Potassium and argon would be anomalies in a periodic table in which elements are arranged in order of increasing atomic weights. Identify two other elements among the transition elements whose positions in the periodic table would have been reversed in a “weight-sequence” arrangement. Which pair of elements would most obviously be out of place on the basis of their chemical behavior? Explain your answer in terms of the current atomic model, showing electron configurations for these elements.
92. ▲ The second ionization energy for magnesium is 1451 kJ/mol. How much energy, in kilojoules, must be absorbed by 1.75 g of gaseous magnesium atoms to convert them to gaseous Mg^{2+} ions?
93. The chemical reactivities of carbon and lead are similar, but there are also major differences. Using their electron configurations, explain why these similarities and differences may exist.

Beyond the Textbook

NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.*

94. Go to the web and locate “MSDS Data Sheets.” Find the MSDS for sodium nitrate. (a) What does LDLo stand for? (b) What does mus stand for?
95. While at the MSDS sheet for sodium nitrate required for Exercise 94, answer the following: (a) What does the Risk Phrase “R8” indicate? (b) What does the Safety Phrase “S39” indicate?
96. Go to http://www.nist.gov/pml/data/ion_energy.cfm and locate values given for the first ionization energies for Al and P. Are the values different than those given in Table 5-1? Explain.
97. ▲ Use the *Handbook of Chemistry and Physics* or a suitable website to find the Crystal Ionic Radii of the Elements. Plot atomic number versus radius of the $2+$ ions of the first d -transition series. Is there a trend? Is a minimum size formed during the transition from Sc^{2+} to Zn^{2+} ? Do the values for the second and third d -transition series appear to form a similar minimum at about the same group number?

Some Types of Chemical Reactions

6



Pouring a solution of silver nitrate, AgNO_3 , into a solution of potassium iodide, KI , produces an immediate precipitate of silver iodide, AgI . The potassium nitrate, KNO_3 , is soluble and remains in solution.

George G. Stanley

OUTLINE

- 6-1 Aqueous Solutions: An Introduction
- 6-2 Reactions in Aqueous Solutions

Naming Some Inorganic Compounds

- 6-3 Naming Binary Compounds
- 6-4 Naming Ternary Acids and Their Salts

Classifying Chemical Reactions

- 6-5 Oxidation–Reduction Reactions: Introduction
- 6-6 Combination Reactions
 - 1 Element + Element $\longrightarrow$ Compound
 - 2 Compound + Element $\longrightarrow$ Compound
 - 3 Compound + Compound $\longrightarrow$ Compound
- 6-7 Decomposition Reactions
 - 1 Compound $\longrightarrow$ Element + Element
 - 2 Compound $\longrightarrow$ Compound + Element
 - 3 Compound $\longrightarrow$ Compound + Compound
- 6-8 Displacement Reactions
 - 1 $\left[\begin{array}{l} \text{More Active Metal +} \\ \text{Salt of Less Active} \\ \text{Metal} \end{array} \right] \longrightarrow \left[\begin{array}{l} \text{Less Active Metal +} \\ \text{Salt of More Active Metal} \end{array} \right]$
 - 2 $\left[\begin{array}{l} \text{Active Metal +} \\ \text{Nonoxidizing Acid} \end{array} \right] \longrightarrow \left[\begin{array}{l} \text{Hydrogen + Salt of Acid} \end{array} \right]$
 - 3 $\left[\begin{array}{l} \text{Active Nonmetal +} \\ \text{Salt of Less Active} \\ \text{Nonmetal} \end{array} \right] \longrightarrow \left[\begin{array}{l} \text{Less Active Nonmetal +} \\ \text{Salt of More Active} \\ \text{Nonmetal} \end{array} \right]$
- 6-9 Metathesis Reactions
 - 1 Acid–Base (Neutralization) Reactions: Formation of a Nonelectrolyte
 - 2 Precipitation Reactions
- 6-10 Gas-Formation Reactions
- 6-11 Summary of Reaction Types

Unless otherwise noted, all content on this page is © Cengage Learning.

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Recognize and describe nonelectrolytes, strong electrolytes, and weak electrolytes
- ▶ Recognize and classify acids (strong, weak), bases (strong, weak, insoluble), and salts (soluble, insoluble); use the solubility guidelines
- ▶ Describe reactions in aqueous solutions by writing formula unit equations, total ionic equations, and net ionic equations
- ▶ Name and write formulas for common binary and ternary inorganic compounds
- ▶ Recognize oxidation–reduction reactions and identify which species are oxidized, reduced, oxidizing agents, and reducing agents
- ▶ Recognize and describe classes of reactions: decomposition reactions, displacement reactions, various types of metathesis reactions, and gas-formation reactions

In this chapter we examine some types of chemical reactions. Millions of reactions are known, so it is useful to group them into classes, or types, so that we can deal systematically with them. We describe whether or not compounds dissolve in water to make aqueous solutions and how these solutions behave, including how well they conduct electricity. We introduce several ways to represent chemical reactions in aqueous solution—formula unit equations, total ionic equations, and net ionic equations—and the advantages and disadvantages of these methods. We also introduce systematic ways to describe chemical reactions, as well as their reactants and their products.

6-1 Aqueous Solutions: An Introduction

Approximately three-fourths of the earth's surface is covered with water. The body fluids of all plants and animals are mainly water. Thus we can see that many important chemical reactions occur in aqueous (water) solutions or in contact with water. In Chapter 3, we introduced solutions and methods of expressing concentrations of solutions. It is useful to know the kinds of substances that are soluble in water, and the forms in which they exist, before we begin our systematic study of chemical reactions.

▶ Positively charged ions are called *cations*, and negatively charged ions are called *anions* (see Section 2-2). The formula for a salt may include H or OH, but it *must* contain another cation and another anion. For example, NaHSO_4 and $\text{Al}(\text{OH})_2\text{Cl}$ are salts, but NaOH and Na_2O are not.

Many substances that interact with water are classified as acids, bases, and salts. An **acid** can be defined as a substance that produces hydrogen ions, H^+ , in aqueous solutions. We usually write the formulas of inorganic acids with hydrogen written first. Organic acids can often be recognized by the presence of the COOH group in the formula. Many properties of aqueous solutions of acids are due to $\text{H}^+(\text{aq})$ ions. These are described in Section 10-4. A **base** is a substance that produces hydroxide ions, OH^- , in aqueous solutions. Acids and bases are further identified in Subsections 2, 3, and 4. A **salt** is an ionic compound that contains a cation other than H^+ and an anion other than hydroxide ion, OH^- , or oxide ion, O^{2-} (see Table 2-2). As we will see later in this chapter, salts are formed when acids react with bases.

1 Electrolytes and Extent of Ionization

Dissociation refers to the process in which a solid *ionic compound*, such as NaCl , separates into its ions in solution:



Molecular compounds, for example *pure* HCl , exist as discrete molecules and do not contain ions; however, many such compounds form ions in solution. **Ionization** refers to the process in which a *molecular compound* separates or reacts with water to form ions in solution:



▶ To give a more complete description of reactions, we indicate the physical states of reactants and products: (g) for gases, (l) for liquids, and (s) for solids. The notation (aq) following ions indicates that they are hydrated in aqueous solution; that is, they interact with water molecules in solution. The complete ionization of a strong electrolyte is indicated by a single arrow ($\longrightarrow$).

Unless otherwise noted, all content on this page is © Cengage Learning.

Solutes that are water-soluble can be classified as either electrolytes or nonelectrolytes.

Electrolytes are substances whose aqueous solutions conduct electric current. **Strong electrolytes** are substances that conduct electricity well in dilute aqueous solution. **Weak electrolytes** conduct electricity poorly in dilute aqueous solution. Aqueous solutions of **nonelectrolytes** do not conduct electricity.

Electric current is carried through aqueous solution by the movement of ions. The strength of an electrolyte depends on the number of ions in solution and also on the charges on these ions (Figure 6-1).

Three major classes of solutes are strong electrolytes: (1) strong acids, (2) strong bases, and (3) most soluble salts. *These compounds are completely or nearly completely ionized or dissociated in aqueous solution.*

► Pure water does not conduct electricity; it is an electrical insulator.

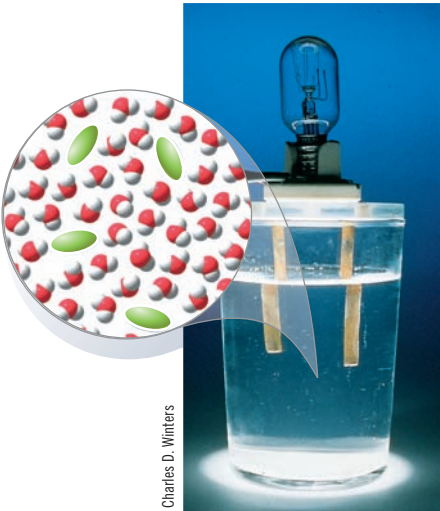
► Recall that ions are charged particles. The movement of charged particles conducts electricity.

2 Strong and Weak Acids

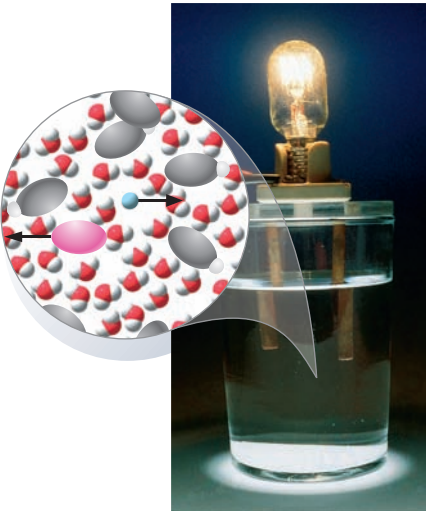
As a matter of convenience we place acids into two classes: strong acids and weak acids. **Strong acids** ionize (separate into hydrogen ions and stable anions) completely, or very nearly completely, in dilute aqueous solution. Seven strong acids and their anions are listed in Table 6-1. Please learn this short list; you can then assume that other acids you encounter are weak.

Because strong acids ionize completely or very nearly completely in dilute solutions, their solutions contain predominantly ions rather than acid molecules. Consider the ionization of hydrochloric acid. Pure hydrogen chloride, HCl, is a molecular compound that is a gas at

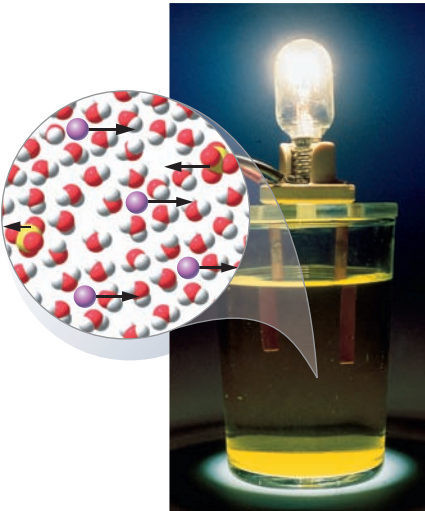
						
H ₂ O molecule	Sugar molecule	Hydrogen ion, H ⁺	Acetic acid molecule, CH ₃ COOH	Acetate ion, CH ₃ COO ⁻	Potassium ion, K ⁺	Chromate ion, CrO ₄ ²⁻



A Pure water and sugar are nonelectrolytes; the absence of ions means that no electricity is conducted, so the bulb does not glow.



B An aqueous solution of a weak electrolyte, acetic acid (CH₃COOH); it contains low concentrations of ions, so the bulb glows dimly.



C An aqueous solution of a strong electrolyte, potassium chromate (K₂CrO₄); it contains a high concentration of ions due to complete dissociation to generate 2K⁺ and CrO₄²⁻ ions, so the bulb glows brightly.

Figure 6-1 An experiment to demonstrate the presence of ions in an aqueous solution. Two metal electrodes are dipped into a liquid in a beaker. When the liquid contains significant concentrations of ions, the ions move between the electrodes to complete the circuit (which includes a light bulb).

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 6-1 The Common Strong Acids and Their Anions

Common Strong Acids		Anions of These Strong Acids	
Formula	Name	Formula	Name
HCl	hydrochloric acid	Cl ⁻	chloride ion
HBr	hydrobromic acid	Br ⁻	bromide ion
HI	hydroiodic acid	I ⁻	iodide ion
HNO ₃	nitric acid	NO ₃ ⁻	nitrate ion
HClO ₄	perchloric acid	ClO ₄ ⁻	perchlorate ion
HClO ₃	chloric acid	ClO ₃ ⁻	chlorate ion
H ₂ SO ₄	sulfuric acid	$\left\{ \begin{array}{l} \text{HSO}_4^- \\ \text{SO}_4^{2-} \end{array} \right.$	hydrogen sulfate ion sulfate ion

► Chloric acid is sometimes not listed with the common strong acids since it is not commonly encountered. However, its anion is much more common. So we have included both the acid and its anion in this table.

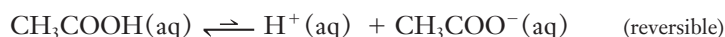
room temperature and atmospheric pressure. When it dissolves in water, it reacts essentially completely to produce a solution that contains hydrogen ions and chloride ions:



Similar equations can be written for all strong acids.

Weak acids ionize only slightly (usually less than 5%) in dilute aqueous solution. Some common weak acids are listed in Appendix F. Several of them and their anions are given in Table 6-2.

The equation for the ionization of acetic acid, CH₃COOH, in water is typical of weak acids:



► Acetic acid is the most familiar organic acid.

► The names given in Table 6-2 correspond to the aqueous solutions.



Citric acid



Citrus fruits contain citric acid, so their juices are acidic. This is shown here by the red colors on the indicator paper. Acids taste sour.

Table 6-2 Some Common Weak Acids and Their Anions

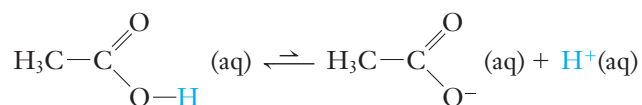
Common Weak Acids		Anions of These Weak Acids	
Formula	Name	Formula	Name
HF*	hydrofluoric acid	F ⁻	fluoride ion
CH ₃ COOH	acetic acid	CH ₃ COO ⁻	acetate ion
HCN	hydrocyanic acid	CN ⁻	cyanide ion
HNO ₂ [†]	nitrous acid	NO ₂ ⁻	nitrite ion
H ₂ CO ₃ [†]	carbonic acid	HCO ₃ ⁻ CO ₃ ²⁻	hydrogen carbonate ion carbonate ion
H ₂ SO ₃ [†]	sulfurous acid	HSO ₃ ⁻ SO ₃ ²⁻	hydrogen sulfite ion sulfite ion
H ₃ PO ₄	phosphoric acid	H ₂ PO ₄ ⁻ HPO ₄ ²⁻ PO ₄ ³⁻	dihydrogen phosphate ion hydrogen phosphate ion phosphate ion
(COOH) ₂	oxalic acid	H(COO) ₂ ⁻ (COO) ₂ ²⁻	hydrogen oxalate ion oxalate ion

*HF is a weak acid, whereas HCl, HBr, and HI are strong acids.

[†]Free acid molecules exist only in dilute aqueous solution or not at all. Many salts of these acids are common, stable compounds, however.

The double arrow $\rightleftharpoons$ generally signifies that the reaction occurs in *both* directions; the longer arrow indicates the direction in which the reaction is favored (in this case the reactants). All of us are familiar with solutions of acetic acid. Vinegar is 5% acetic acid by mass. Our use of oil and vinegar as a salad dressing suggests that acetic acid is a weak acid; we could not safely drink a 5% solution of any strong acid. To be specific, acetic acid is 0.5% ionized (and 99.5% nonionized) in 5% solution.

A multitude of organic acids occur in living systems. Organic acids contain the carboxyl grouping of atoms, —COOH . Most common organic acids are weak. They can ionize slightly by breaking the O—H bond to form the carboxylate group, —COO^- , as shown for acetic acid:

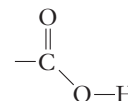


Organic acids are discussed in Chapter 23. Some naturally occurring organic weak acids are tartaric acid (grapes), lactic acid (sour milk), and formic acid (ants). Carbonic acid, H_2CO_3 , and hydrocyanic acid, HCN(aq) , are two common acids that contain carbon but that are considered to be *inorganic* acids. Inorganic acids are often called **mineral acids** because they are obtained primarily from nonliving sources.

► We will learn more about acids in Chapter 10. There we will see that it is appropriate to represent $\text{H}^+\text{(aq)}$ as H_3O^+ to emphasize its interaction with water.

► Our stomachs have linings that are much more resistant to attack by acids than are our other tissues.

► The carboxyl group —COOH is



► Other organic acids have different groups in the position of the $\text{H}_3\text{C—}$ group in acetic acid. The double line linking C to one O represents a double bond, which is stronger than a single bond.

EXAMPLE 6-1 Strong and Weak Acids

In the following lists of common acids, which are strong and which are weak? (a) H_3PO_4 , HCl , H_2CO_3 , HNO_3 ; (b) HClO_4 , H_2SO_4 , HClO , HF .

Plan

We recall that Table 6-1 lists some common strong acids. Other *common* acids are assumed to be weak.

Solution

(a) HCl and HNO_3 are strong acids; H_3PO_4 and H_2CO_3 are weak acids.

(b) HClO_4 and H_2SO_4 are strong acids; HClO and HF are weak acids.

You should now work Exercises 5 and 7.

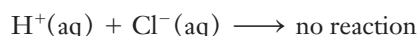
► Inorganic acids may be strong or weak.



Many common food and household products are acidic (orange juice, vinegar, soft drinks, citrus fruits) or basic (cleaning preparations, baking soda).

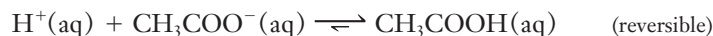
3 Reversible Reactions

Reactions that occur in both directions are **reversible reactions**. We use a double arrow $\rightleftharpoons$ to indicate that a reaction is *reversible*. Chemists often qualitatively indicate the favored direction of a reversible reaction by using a longer arrow. Equal length arrows, however, do not mean that there are equal amounts of reactant and product. The favored direction and extent of the reaction is described quantitatively by the equilibrium constant (see Chapter 17). What is the fundamental difference between reactions that go to completion and those that are reversible? We have seen that HCl ionizes completely in water. Suppose we dissolve some table salt, NaCl , in water and then add some dilute nitric acid to it. The resulting solution contains Na^+ and Cl^- ions (from the dissociation of NaCl) as well as H^+ and NO_3^- (from the ionization of HNO_3). The H^+ and Cl^- ions do *not* react significantly to form nonionized HCl molecules; this would be the reverse of the ionization of HCl .



► Na^+ and NO_3^- ions do not combine because NaNO_3 is a soluble ionic compound.

In contrast, when a sample of sodium acetate, NaCH_3COO , is dissolved in H_2O and mixed with nitric acid, the resulting solution initially contains Na^+ , CH_3COO^- , H^+ , and NO_3^- ions. But most of the H^+ and CH_3COO^- ions combine to produce nonionized molecules of acetic acid, the reverse of the ionization of the acid. Thus, the ionization of acetic acid, like that of any other weak electrolyte, is reversible.



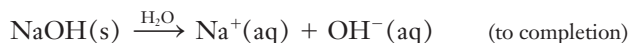
► Solutions of bases have a set of common properties due to the OH^- ion. These are described in Section 10-4.

► Strong bases are ionic compounds in the solid state.

► The weak bases are *molecular* substances that dissolve in water to give slightly basic solutions; they are sometimes called molecular bases.

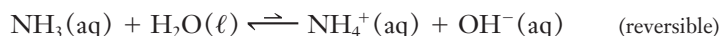
4 Strong Bases, Insoluble Bases, and Weak Bases

Most common bases are *ionic* metal hydroxides. **Strong bases** are soluble in water and are dissociated completely in dilute aqueous solution. The common strong bases are listed in Table 6-3. They are the hydroxides of the Group 1A metals and the heavier members of Group 2A. The equation for the dissociation of sodium hydroxide in water is typical. Similar equations can be written for other strong bases.

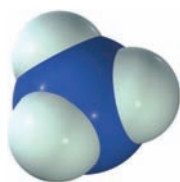


Other metals form ionic hydroxides, but these are so sparingly soluble in water that they cannot produce strongly basic solutions. They are called **insoluble bases** or sometimes sparingly soluble bases. Typical examples include $\text{Cu}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Fe}(\text{OH})_2$, and $\text{Fe}(\text{OH})_3$.

Common **weak bases** are molecular substances that are soluble in water but form only low concentrations of ions in solution. The most common weak base is ammonia, NH_3 .



Closely related N-containing compounds, the *amines*, such as methylamine, CH_3NH_2 , and aniline, $\text{C}_6\text{H}_5\text{NH}_2$, are also weak bases. Nicotine (found in tobacco) and caffeine (found in coffee, tea, and cola drinks) are naturally occurring amines.



Ammonia, NH_3

EXAMPLE 6-2 Classifying Bases

From the following lists, choose (i) the strong bases, (ii) the insoluble bases, and (iii) the weak bases. (a) NaOH , $\text{Cu}(\text{OH})_2$, $\text{Pb}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$; (b) $\text{Fe}(\text{OH})_3$, KOH , $\text{Mg}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, NH_3 .

Plan

(i) We recall that Table 6-3 lists the *common strong bases*. (ii) Other common metal hydroxides are assumed to be *insoluble bases*. (iii) Ammonia and closely related nitrogen-containing compounds, the amines, are the common *weak bases*.

Solution

- (a) (i) The strong bases are NaOH and $\text{Ba}(\text{OH})_2$, so
 (ii) The insoluble bases are $\text{Cu}(\text{OH})_2$ and $\text{Pb}(\text{OH})_2$.
 (b) (i) The strong bases are KOH and $\text{Sr}(\text{OH})_2$, so
 (ii) The insoluble bases are $\text{Fe}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$, and
 (iii) The weak base is NH_3 .

You should now work Exercises 8 and 10.

Table 6-3 The Common Strong Bases

Group 1A		Group 2A	
LiOH	lithium hydroxide		
NaOH	sodium hydroxide		
KOH	potassium hydroxide	Ca(OH) ₂	calcium hydroxide
RbOH	rubidium hydroxide	Sr(OH) ₂	strontium hydroxide
CsOH	cesium hydroxide	Ba(OH) ₂	barium hydroxide

5 Solubility Guidelines for Compounds in Aqueous Solution

Solubility is a complex phenomenon, and it is not possible to give a complete summary of all our observations. The following brief summary for solutes in aqueous solutions will be very useful. These generalizations are often called the *solubility guidelines*. Compounds whose solubility in water is less than about 0.02 mol/L are usually classified as insoluble compounds, whereas those that are more soluble are classified as soluble compounds. No gaseous or solid substances are infinitely soluble in water. You may wish to review Tables 2-2, 6-1, and 6-2. They list some common ions. Table 6-6 contains a more comprehensive list.

► There is no sharp dividing line between “soluble” and “insoluble” compounds. Compounds whose solubilities fall near the arbitrary division are called “moderately soluble” compounds.

1. The common inorganic acids are soluble in water. Low-molecular-weight organic acids are also soluble.
2. All common compounds of the Group 1A metal ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and the ammonium ion, NH_4^+ , are soluble in water.
3. The common nitrates, NO_3^- ; acetates, CH_3COO^- ; chlorates, ClO_3^- ; and perchlorates, ClO_4^- , are soluble in water.
4. (a) The common chlorides, Cl^- , are soluble in water except AgCl , Hg_2Cl_2 , and PbCl_2 .
(b) The common bromides, Br^- , and iodides, I^- , show approximately the same solubility behavior as chlorides, but there are some exceptions. As these halide ions (Cl^- , Br^- , I^-) increase in size, the solubilities of their slightly soluble compounds decrease.
(c) The common fluorides, F^- , are soluble in water except MgF_2 , CaF_2 , SrF_2 , BaF_2 , and PbF_2 .
5. The common sulfates, SO_4^{2-} , are soluble in water except PbSO_4 , BaSO_4 , and HgSO_4 ; CaSO_4 , SrSO_4 , and Ag_2SO_4 are moderately soluble.
6. The common metal hydroxides, OH^- , are *insoluble* in water except those of the Group 1A metals and the heavier members of the Group 2A metals, beginning with $\text{Ca}(\text{OH})_2$.
7. The common carbonates, CO_3^{2-} , phosphates, PO_4^{3-} , and arsenates, AsO_4^{3-} , are *insoluble* in water except those of the Group 1A metals and NH_4^+ . MgCO_3 is moderately soluble.
8. The common sulfides, S^{2-} , are *insoluble* in water except those of the Group 1A and Group 2A metals and the ammonium ion.

Table 6-4 summarizes much of the information about the solubility guidelines.



© Bob Krist/Corbis

The White Cliffs of Dover, England, are composed mainly of calcium carbonate (CaCO_3).

Table 6-4 Solubility Guidelines for Common Ionic Compounds in Water

Generally Soluble	Exceptions
Na^+ , K^+ , NH_4^+ compounds	No common exceptions
fluorides (F^-)	Insoluble: MgF_2 , CaF_2 , SrF_2 , BaF_2 , PbF_2
chlorides (Cl^-)	Insoluble: AgCl , Hg_2Cl_2 Soluble in hot water: PbCl_2
bromides (Br^-)	Insoluble: AgBr , Hg_2Br_2 , PbBr_2 Moderately soluble: HgBr_2
iodides (I^-)	Insoluble: many heavy-metal iodides
sulfates (SO_4^{2-})	Insoluble: BaSO_4 , PbSO_4 , HgSO_4 Moderately soluble: CaSO_4 , SrSO_4 , Ag_2SO_4
nitrates (NO_3^-), nitrites (NO_2^-)	Moderately soluble: AgNO_2
chlorates (ClO_3^-), perchlorates (ClO_4^-)	No common exceptions
acetates (CH_3COO^-)	Moderately soluble: AgCH_3COO
Generally Insoluble	Exceptions
sulfides (S^{2-})	Soluble [†] : those of NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}
oxides (O^{2-}), hydroxides (OH^-)	Soluble: Li_2O^* , LiOH , Na_2O^* , NaOH , K_2O^* , KOH , BaO^* , $\text{Ba}(\text{OH})_2$ Moderately soluble: CaO^* , $\text{Ca}(\text{OH})_2$, SrO^* , $\text{Sr}(\text{OH})_2$
carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), arsenates (AsO_4^{3-})	Soluble: those of NH_4^+ , Na^+ , K^+

*Dissolves with evolution of heat and formation of hydroxides.

[†]Dissolves with formation of HS^- and H_2S .

EXAMPLE 6-3 Solubility of Some Common Ionic Compounds

From the following compounds, choose (a) those that are likely to be soluble in water and (b) those that are likely to be insoluble: NaBr , $\text{Cu}(\text{OH})_2$, PbCl_2 , AgI , Fe_2O_3 , $\text{Mg}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{SO}_4$.

Plan

We recall from the guidelines and Table 6-4 that all Na^+ , K^+ , and NH_4^+ salts are soluble. Therefore, we predict that NaBr and $(\text{NH}_4)_2\text{SO}_4$ will be soluble. Similarly, NO_3^- salts are soluble, so $\text{Mg}(\text{NO}_3)_2$ should also be soluble. All other compounds listed in this example should be insoluble.

Solution

(a) The soluble compounds are NaBr , $(\text{NH}_4)_2\text{SO}_4$, and $\text{Mg}(\text{NO}_3)_2$.

(b) The insoluble compounds are $\text{Cu}(\text{OH})_2$, PbCl_2 , AgI , and Fe_2O_3 .

You should now work Exercises 14 and 16.



Problem-Solving Tip Solubility Guidelines and Charges on Ions

To help understand the solubility rules for ionic compounds, think about the magnitudes of the charges on the cation and anion. The higher the charges are, the more strongly the anion and cation attract one another and the less soluble the salt is likely to be. For example, almost all salts composed of $1+$ cations and $1-$ anions are soluble (Ag^+ salts are a notable exception). Almost all salts composed of $2+/2-$ and $3+/3-$ ion pairs are insoluble (or only slightly soluble).

The situation is a little more complicated with mixed charge combinations, but you can always estimate the force of ionic attraction between the anion and cation by multiplying the absolute values of their charges. Larger numbers indicate stronger attractive forces and suggest lower solubility.

For example, Na_3PO_4 has a $1+$ charged cation and a $3-$ charged anion giving a relative ionic attractive force of 3 (you use only *one* Na^+ in this multiplication, not the three needed to balance the charge on the anion). CaSO_4 ($2+/2-$ combination) has a relative ionic attractive force of 4, while $\text{Ca}_3(\text{PO}_4)_2$ ($2+/3-$ combination) has a relative attractive force of 6. The solubility of these compounds is as follows (greatest to least soluble): $\text{Na}_3\text{PO}_4 > \text{CaSO}_4 > \text{Ca}_3(\text{PO}_4)_2$.

The size of the ions is also a factor, with smaller ions able to get closer to one another and thus increase the ionic attractive force. This is why larger anions with low negative charges almost always give soluble salts (e.g., NO_3^- or ClO_4^-). These ionic charge and size considerations are based on Coulomb's Law (discussed in Chapter 13).

You may wonder about the trend for AgCl , AgBr , and AgI , where the solubility decreases despite the increasing size of the anions. Transition metal compounds often involve dative bonding (see Section 10-10 and Chapter 25), which is a weaker form of covalent bonding, between the cation and anion. Dative bonding generally increases with donor strength: $\text{I}^- > \text{Br}^- > \text{Cl}^-$.

STOP & THINK

This problem-solving tip is based on the simple fundamental concept that opposite charges attract. Higher and more concentrated charges have stronger attractive forces that can resist the solution process that pulls the ions apart. Further, transition metal and heavier main group metalloid cations form stronger bonds to most anions. You can use these concepts to explain most of the solubility trends.

We have distinguished between strong and weak electrolytes and between soluble and insoluble compounds. Let us now see how we can describe chemical reactions in aqueous solutions.

6-2 Reactions in Aqueous Solutions

Many important chemical reactions occur in aqueous solutions. In this chapter you will learn to describe such aqueous reactions and to predict the products of many reactions.

First, let's look at how we write chemical equations that describe reactions in aqueous solutions. We use three kinds of chemical equations. Table 6-5 shows the kinds of information about each substance that we use in writing equations for reactions in aqueous solutions. Some typical examples are included. Refer to Table 6-5 often as you study the following sections.

Table 6-5 Bonding, Solubility, Electrolyte Characteristics, and Predominant Forms of Solutes in Contact with Water

	Acids		Bases			Salts	
	Strong Acids	Weak Acids	Strong Bases	Insoluble Bases	Weak Bases	Soluble Salts	Insoluble Salts
Examples	HCl HNO_3	CH_3COOH HF	NaOH $\text{Ca}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$ $\text{Al}(\text{OH})_3$	NH_3 CH_3NH_2	KCl , NaNO_3 , NH_4Br	BaSO_4 , AgCl , $\text{Ca}_3(\text{PO}_4)_2$
Pure compound ionic or molecular?	Molecular	Molecular	Ionic	Ionic	Molecular	Ionic	Ionic
Water-soluble or insoluble?	Soluble*	Soluble*	Soluble	Insoluble	Soluble†	Soluble	Insoluble
≈ 100% ionized or dissociated in dilute aqueous solution?	Yes	No	Yes	(footnote‡)	No	Yes§	(footnote‡)
Written in ionic equations as	Separate ions	Molecules	Separate ions	Complete formulas	Molecules	Separate ions	Complete formulas

*Most common inorganic acids and the low-molecular-weight organic acids ($-\text{COOH}$) are water-soluble.

†The low-molecular-weight amines are water-soluble.

‡The *very small concentrations* of “insoluble” metal hydroxides and insoluble salts in saturated aqueous solutions are nearly completely dissociated.

§There are a few exceptions. A few soluble salts are molecular (and not ionic) compounds.

Unless otherwise noted, all content on this page is © Cengage Learning.

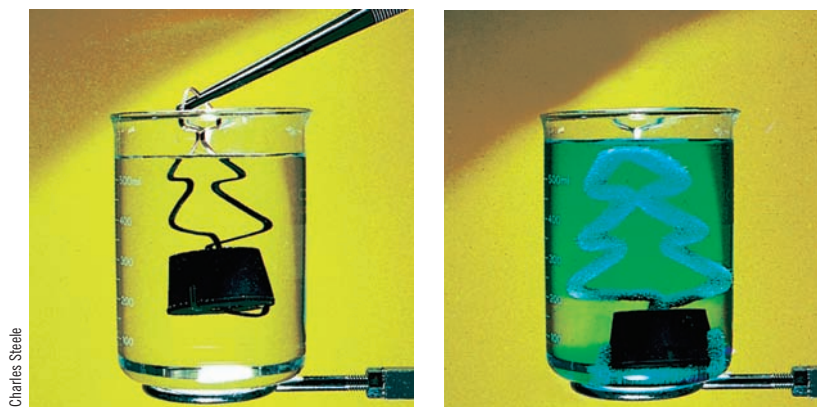


Figure 6-2 Reaction of Cu(s) and Ag⁺(aq).

A Copper wire and a silver nitrate solution

B The copper wire has been placed in the solution and some finely divided silver has deposited on the wire. The solution is blue because it contains copper(II) nitrate.

► Because we have not studied periodic trends in properties of transition metals, you might not be able to predict that Cu is more active than Ag. The fact that this reaction occurs (see Figure 6-2) shows that it is.

► Ions that appear in the same form in solution on both sides of the total ionic equation are called **spectator ions**; they undergo no change in the chemical reaction.

► Brackets are not used in net ionic equations.

► This is why it is important to know how and when to construct net ionic equations from formula unit equations.

STOP & THINK

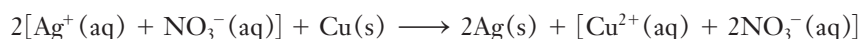
The only common substances that should be written as ions in ionic equations are (1) strong acids, (2) strong bases, and (3) soluble salts. You must also remember the common polyatomic ions, their charges, and that they are units that do not typically dissociate further (e.g., PO₄³⁻, SO₄²⁻, CO₃²⁻).

1. In formula unit equations, we show complete formulas for all compounds. When metallic copper is added to a solution of (colorless) silver nitrate, the more active metal—copper—displaces silver ions from the solution. The resulting solution contains blue copper(II) nitrate, and metallic silver forms as a finely divided solid (Figure 6-2):



Both silver nitrate and copper(II) nitrate are soluble ionic compounds (for solubility guidelines see Table 6-4 and Section 6-1, Part 5).

2. In total ionic equations, formulas are written to show the (predominant) form in which each substance exists when it is in contact with aqueous solution. We sometimes use brackets in total ionic equations to show ions that have a common source or that remain in solution after the reaction is complete. The total ionic equation for this reaction is



Examination of the total ionic equation shows that NO₃⁻ ions do not participate in the reaction. Because they do not change, they are often called “spectator” ions.

3. In **net ionic equations**, we show only the species that react. The net ionic equation is obtained by eliminating the spectator ions and the brackets from the total ionic equation.



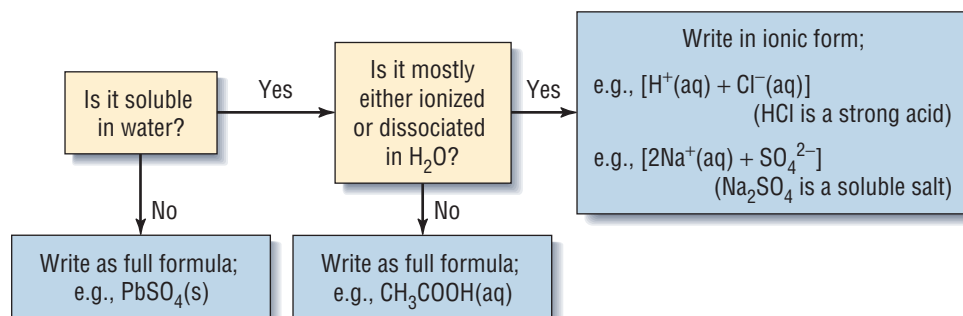
Net ionic equations allow us to focus on the *essence* of a chemical reaction in aqueous solutions. On the other hand, if we are dealing with stoichiometric calculations, we frequently must deal with formula weights and therefore with the *complete* formulas of all species. In such cases, formula unit equations are more useful. Total ionic equations provide the bridge between the two.

Problem-Solving Tip Writing Ionic Equations

The following chart will help in deciding which formula units are to be written as separate ions in the total ionic equation and which ones are to be written as unchanged formula units. You must answer two questions about a substance to determine whether it should be written in ionic form or as a formula unit in the total and net ionic equations.

1. Does it dissolve in water? If not, write the full formula.
2. (a) If it dissolves, does it ionize (a strong acid)?
(b) If it dissolves, does it dissociate (a strong base or a soluble salt)?

If the answer to *either part* of the second question is yes, the substance is a soluble strong electrolyte, and its formula is written in ionic form.



Recall the lists of strong acids (see Table 6-1) and strong bases (see Table 6-3). These acids and bases are completely or almost completely ionized or dissociated in dilute aqueous solutions. Other common acids and bases are either insoluble or only slightly ionized or dissociated. In addition, the solubility guidelines (see Table 6-4 and Section 6-1, Part 5) allow you to determine which salts are soluble in water. Most salts that are soluble in water are also strong electrolytes. Exceptions such as lead acetate, $\text{Pb}(\text{CH}_3\text{COO})_2$, which is soluble but does not ionize appreciably, will be noted as they are encountered.

Naming Some Inorganic Compounds

The rules for naming compounds are determined by the Committee on Inorganic Nomenclature of the International Union of Pure and Applied Chemistry (IUPAC). The names and formulas of a few organic compounds were given in Table 2-1, and more systematic rules for naming them will appear in Chapter 23.

6-3 Naming Binary Compounds

A **binary compound** consists of two elements; it may be either ionic or molecular. The rule is to name the less electronegative element first and the more electronegative element second. The more electronegative element will have a negative oxidation state and is named by adding an “-ide” suffix to the element’s *unambiguous* stem. Stems for the nonmetals follow.

3A	4A	5A	6A	7A
B bor	C carb Si silic	N nitr P phosph As arsen Sb antimon	O ox S sulf Se selen Te tellur	H hydr F fluor Cl chlor Br brom I iod

► Millions of compounds are known, so it is important to be able to associate names and formulas in a systematic way.

► The stem for each element is derived from the name of the element.

Binary ionic compounds contain metal cations and nonmetal anions. The cation is named first and the anion second.

Formula	Name	Formula	Name
KBr	potassium bromide	Rb ₂ S	rubidium sulfide
CaCl ₂	calcium chloride	Ba ₃ N ₂	barium nitride
NaH	sodium hydride	SrO	strontium oxide

► Notice that there is a space between the name of the cation and the name of the anion.

The preceding method is sufficient for naming binary ionic compounds containing metals that exhibit *only one oxidation state* other than zero (see Section 6-3). Most transition metals and the metals of Groups 3A (except Al), 4A, and 5A exhibit more than one oxidation state. These metals may form two or more binary compounds with the same nonmetal. To distinguish among all the possibilities, the oxidation state of the metal is

► Roman numerals are *not* necessary for metals that commonly exhibit only one oxidation state in their compounds.

Unless otherwise noted, all content on this page is © Cengage Learning.

indicated by a Roman numeral in parentheses following its name. This method can be applied to any binary compound of a metal and a nonmetal.

► Notice that prefixes are not used to indicate the number of ions in the formula.

Oxidation State			Oxidation State		
Formula	of Metal	Name	Formula	of Metal	Name
Cu ₂ O	+1	copper(I) oxide	FeBr ₂	+2	iron(II) bromide
CuF ₂	+2	copper(II) fluoride	Fe(NO ₃) ₂	+3	iron(III) nitrate
FeS	+2	iron(II) sulfide	Hg ₂ Cl ₂	+1	mercury(I) chloride
Fe ₂ O ₃	+3	iron(III) oxide	HgCl ₂	+2	mercury(II) chloride

The advantage of the IUPAC system is that if you know the formula, you can write the exact and unambiguous name; if you are given the name, you can write the formula at once. An older method, still in use but not recommended by the IUPAC, uses “-ous” and “-ic” suffixes to indicate lower and higher oxidation states, respectively. This system can distinguish between only two different oxidation states for a metal. It is therefore not as useful as the Roman numeral system and we will use it rarely in this book.

► Familiarity with the older system is still necessary. It is still widely used in many scientific, engineering, and medical fields. The most commonly used older cation names are

Cation	IUPAC Name	Older Name
Fe ²⁺	iron(II)	ferrous
Fe ³⁺	iron(III)	ferric
Cu ⁺	copper(I)	cuprous
Cu ²⁺	copper(II)	cupric
Hg ₂ ²⁺	mercury(I)	mercurous
Hg ²⁺	mercury(II)	mercuric

Your instructor may require you to know this short list, as well as others to be specified.

► If you don't already know them, you should learn these common prefixes.

Number	Prefix
2	di
3	tri
4	tetra
5	penta
6	hexa
7	hepta
8	octa
9	nona
10	deca

Oxidation State			Oxidation State		
Formula	of Metal	Name	Formula	of Metal	Name
CuCl	+1	cuprous chloride	FeSO ₄	+2	ferrous sulfate
CuCl ₂	+2	cupric chloride	Fe(NO ₃) ₃	+3	ferric nitrate
FeO	+2	ferrous oxide	Hg ₂ Cl ₂	+1	mercurous chloride
FeBr ₃	+3	ferric bromide	HgCl ₂	+2	mercuric chloride

A list of common cations and anions appears in Table 6-6. It will enable you to name many of the ionic compounds you encounter.

Nearly all **binary molecular compounds** involve two *nonmetals* bonded together, such as PCl₃. Although many nonmetals can exhibit different oxidation states, their oxidation states are *not* properly indicated by Roman numerals or suffixes. Instead, elemental proportions in binary covalent compounds are indicated by using a *prefix* system for both elements. The Greek and Latin prefixes for one through ten are *mono-*, *di-*, *tri-*, *tetra-*, *penta-*, *hexa-*, *hepta-*, *octa-*, *nona-*, and *deca-*. The prefix “mono-” is omitted for both elements except in the common name for CO, carbon monoxide. We use the minimum number of prefixes needed to name a compound unambiguously. The final “a” in a prefix is omitted when the nonmetal stem begins with the letter “o”; we write “heptoxide,” not “heptaoxide.”

Formula	Name	Formula	Name
SO ₂	sulfur dioxide	Cl ₂ O ₇	dichlorine heptoxide
SO ₃	sulfur trioxide	CS ₂	carbon disulfide
N ₂ O ₄	dinitrogen tetroxide	SF ₄	sulfur tetrafluoride
As ₄ O ₆	tetraarsenic hexoxide	SF ₆	sulfur hexafluoride

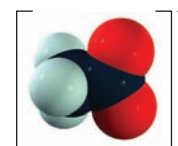
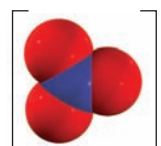
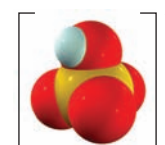
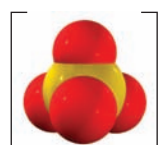
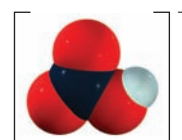
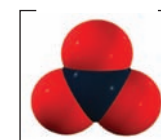
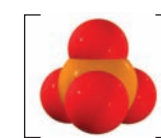
Binary acids are compounds in which H is bonded to a Group 6A element other than O or to a Group 7A element; they act as acids when dissolved in water. *The pure compounds are named as typical binary compounds.* Their aqueous solutions are named by modifying the characteristic stem of the nonmetal with the prefix “hydro-” and the suffix “-ic” followed by the word “acid.” The stem for sulfur in this instance is “sulfur” rather than “sulf.”

Formula	Name of Compound	Name of Aqueous Solution
HCl	hydrogen chloride	hydrochloric acid, HCl(aq)
HF	hydrogen fluoride	hydrofluoric acid, HF(aq)
H ₂ S	hydrogen sulfide	hydrosulfuric acid, H ₂ S(aq)
HCN	hydrogen cyanide	hydrocyanic acid, HCN(aq)

In later chapters we will learn additional systematic rules for naming more complex compounds.

Table 6-6 Formulas and Names for Some Common Ions

Common Cations		Common Anions	
Formula	Name	Formula	Name
Li^+	lithium ion	F^-	fluoride ion
Na^+	sodium ion	Cl^-	chloride ion
K^+	potassium ion	Br^-	bromide ion
NH_4^+	ammonium ion	I^-	iodide ion
Ag^+	silver ion	OH^-	hydroxide ion
		CN^-	cyanide ion
Mg^{2+}	magnesium ion	ClO^-	hypochlorite ion
Ca^{2+}	calcium ion	ClO_2^-	chlorite ion
Ba^{2+}	barium ion	ClO_3^-	chlorate ion
Cd^{2+}	cadmium ion	ClO_4^-	perchlorate ion
Zn^{2+}	zinc ion	CH_3COO^-	acetate ion
Cu^{2+}	copper(II) ion or cupric ion	MnO_4^-	permanganate ion
Hg_2^{2+}	mercury(I) ion or mercurous ion	NO_2^-	nitrite ion
Hg^{2+}	mercury(II) ion or mercuric ion	NO_3^-	nitrate ion
		SCN^-	thiocyanate ion
Mn^{2+}	manganese(II) ion	O^{2-}	oxide ion
Co^{2+}	cobalt(II) ion	S^{2-}	sulfide ion
Ni^{2+}	nickel(II) ion	HSO_3^-	hydrogen sulfite ion or bisulfite ion
Pb^{2+}	lead(II) ion or plumbous ion	SO_3^{2-}	sulfite ion
Sn^{2+}	tin(II) ion or stannous ion	HSO_4^-	hydrogen sulfate ion or bisulfate ion
Fe^{2+}	iron(II) ion or ferrous ion	SO_4^{2-}	sulfate ion
Fe^{3+}	iron(III) ion or ferric ion	HCO_3^-	hydrogen carbonate ion or bicarbonate ion
Al^{3+}	aluminum ion	CO_3^{2-}	carbonate ion
Cr^{3+}	chromium(III) ion or chromic ion	CrO_4^{2-}	chromate ion
		$\text{Cr}_2\text{O}_7^{2-}$	dichromate ion
		PO_4^{3-}	phosphate ion
		AsO_4^{3-}	arsenate ion

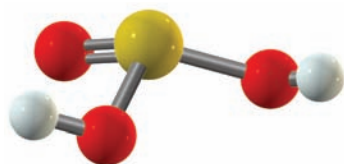
hydroxide ion, OH^- cyanide ion, CN^- acetate ion, CH_3COO^- nitrate ion, NO_3^- bisulfate ion, HSO_4^- sulfate ion, SO_4^{2-} bicarbonate ion, HCO_3^- carbonate ion, CO_3^{2-} dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$ phosphate ion, PO_4^{3-}  SF_4  SF_6

6-4 Naming Ternary Acids and Their Salts

A **ternary compound** consists of three elements. **Ternary acids (oxoacids)** are compounds of hydrogen, oxygen, and (usually) a nonmetal. Nonmetals that exhibit more than one oxidation state form more than one ternary acid. These ternary acids differ in the number of oxygen atoms they contain. The suffixes “-ous” and “-ic” following the stem name of the central element indicate lower and higher oxidation states, respectively. One common ternary acid of each nonmetal is (somewhat arbitrarily) designated as the “-ic” acid. That is, it is named by putting the element stem before the “-ic” suffix. The common ternary “-ic

Unless otherwise noted, all content on this page is © Cengage Learning.

► The oxoacid with the central element in the highest oxidation state usually contains more O atoms. Oxoacids with their central elements in lower oxidation states usually have fewer O atoms.



H_2SO_3 , sulfurous acid



H_2SO_4 , sulfuric acid

► Notice that $\text{H}_2\text{N}_2\text{O}_2$ has a 1:1 ratio of nitrogen to oxygen, as would the hypothetical HNO .

acids” are shown in Table 6-7. It is important to learn the names and formulas of these acids because the names of all other ternary acids and salts are derived from them. There are no common “-ic” ternary acids for the omitted nonmetals.

Acids containing *one fewer oxygen atom* per central atom are named in the same way except that the “-ic” suffix is changed to “-ous.” The oxidation state of the central element is *lower by 2* in the “-ous” acid than in the “-ic” acid.

Formula	Oxidation State	Name	Formula	Oxidation State	Name
H_2SO_3	+4	sulfurous acid	H_2SO_4	+6	sulfuric acid
HNO_2	+3	nitrous acid	HNO_3	+5	nitric acid
H_2SeO_3	+4	selenous acid	H_2SeO_4	+6	selenic acid
HBrO_2	+3	bromous acid	HBrO_3	+5	bromic acid

Ternary acids that have one fewer O atom than the “-ous” acids (two fewer O atoms than the “-ic” acids) are named using the prefix “hypo-” and the suffix “-ous.” These are acids in which the oxidation state of the central nonmetal is *lower by 2* than that of the central nonmetal in the “-ous acids.”

Formula	Oxidation State	Name
HClO	+1	<i>hypochlorous acid</i>
H_3PO_2	+1	<i>hypophosphorous acid</i>
HIO	+1	<i>hypoiodous acid</i>
$\text{H}_2\text{N}_2\text{O}_2$	+1	<i>hyponitrous acid</i>

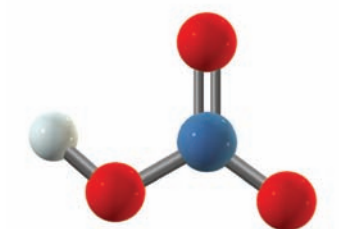
Acids containing *one more oxygen atom* per central nonmetal atom than the normal “-ic acid” are named “*perstemic*” acids.

Formula	Oxidation State	Name
HClO_4	+7	<i>perchloric acid</i>
HBrO_4	+7	<i>perbromic acid</i>
HIO_4	+7	<i>periodic acid</i>

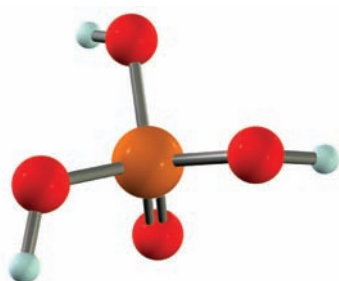
Table 6-7 Formulas of Some “-ic” Acids

Periodic Group of Central Elements				
3A	4A	5A	6A	7A
H_3BO_3 boric acid	H_2CO_3 carbonic acid	HNO_3 nitric acid		
	H_4SiO_4 silicic acid	H_3PO_4 phosphoric acid	H_2SO_4 sulfuric acid	HClO_3 chloric acid
		H_3AsO_4 arsenic acid	H_2SeO_4 selenic acid	HBrO_3 bromic acid
			H_6TeO_6 telluric acid	HIO_3 iodic acid

Note that the oxidation state of the central atom is equal to its periodic group number, except for the halogens.



HNO_3 , nitric acid



H_3PO_4 , phosphoric acid

The oxoacids of chlorine can be summarized as follows:

Formula	Oxidation State	Name
HClO	+1	<i>hypochlorous acid</i>
HClO ₂	+3	<i>chlorous acid</i>
HClO ₃	+5	<i>chloric acid</i>
HClO ₄	+7	<i>perchloric acid</i>

Ternary salts are compounds that result from replacing the hydrogen in a ternary acid with another ion. They usually contain metal cations or the ammonium ion. As with binary compounds, the cation is named first. The name of the anion is based on the name of the ternary acid from which it is derived.

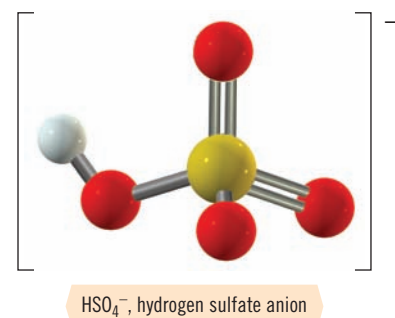
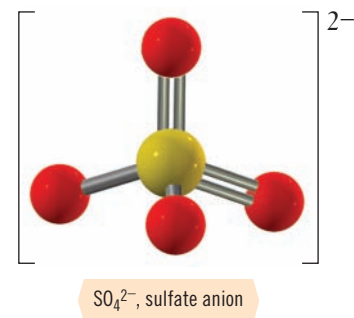
An anion derived from a ternary acid with an “-ic” ending is named by dropping the “-ic acid” and replacing it with “-ate.” An anion derived from an “-ous acid” is named by replacing the suffix “-ous acid” with “-ite.” The “per-” and “hypo-” prefixes are retained.

Formula	Name
(NH ₄) ₂ SO ₄	ammonium sulfate (SO ₄ ²⁻ from sulfuric acid, H ₂ SO ₄)
KNO ₃	potassium nitrate (NO ₃ ⁻ from nitric acid, HNO ₃)
Ca(NO ₂) ₂	calcium nitrite (NO ₂ ⁻ from nitrous acid, HNO ₂)
LiClO ₄	lithium perchlorate (ClO ₄ ⁻ from perchloric acid, HClO ₄)
FePO ₄	iron(III) phosphate (PO ₄ ³⁻ from phosphoric acid, H ₃ PO ₄)
NaClO	sodium hypochlorite (ClO ⁻ from hypochlorous acid, HClO)

Acidic salts contain anions derived from ternary polyprotic acids in which one or more acidic hydrogen atoms remain. These salts are named as if they were the usual type of ternary salt, with the word “hydrogen” or “dihydrogen” inserted after the name of the cation to show the number of acidic hydrogen atoms.

Formula	Name	Formula	Name
NaHSO ₄	sodium hydrogen sulfate	KH ₂ PO ₄	potassium dihydrogen phosphate
NaHSO ₃	sodium hydrogen sulfite	K ₂ HPO ₄	potassium hydrogen phosphate
		NaHCO ₃	sodium hydrogen carbonate

An older, commonly used method (which is not recommended by the IUPAC, but which is widely used in commerce) involves the use of the prefix “bi-” attached to the name of the anion to indicate the presence of an acidic hydrogen. According to this system, NaHSO₄ is called sodium bisulfate and NaHCO₃ is called sodium bicarbonate.



Problem-Solving Tip Naming Ternary Acids and Their Anions

The following table will help you to remember the names of the ternary acids and their ions. First learn the formulas of the acids mentioned earlier that end with “-ic acid.” Then relate possible other acids to the following table. The stem (XXX) represents the stem of the name, for example, “nitr,” “sulfur,” or “chlor.”

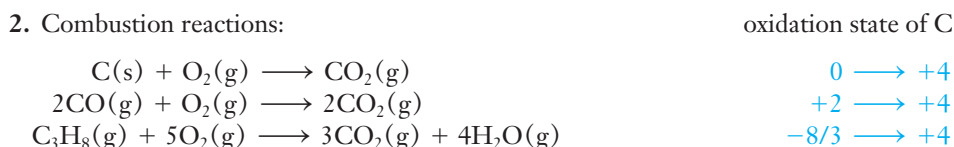
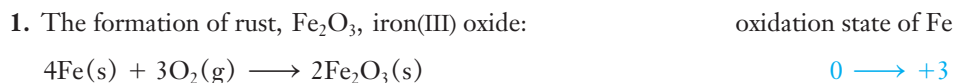
Decreasing number of oxygen atoms on central atom ↓	Ternary Acid	Anion	Decreasing oxidation number of central atom ↓
	perXXXic acid	perXXXate	
	XXXic acid	XXXate	
	XXXous acid	XXXite	
	hypoXXXous acid	hypoXXXite	

Classifying Chemical Reactions

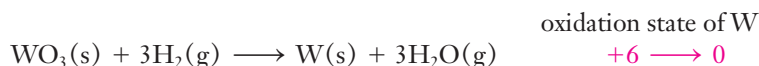
We will now discuss chemical reactions in further detail. We classify them as oxidation–reduction reactions, combination reactions, decomposition reactions, displacement reactions, gas-formation reactions, and metathesis reactions. The last type can be further described as precipitation reactions and acid–base (neutralization) reactions. We will see that many reactions, especially oxidation–reduction reactions, fit into more than one category, and that some reactions do not fit neatly into any of them. As we study different kinds of chemical reactions, we will learn to predict the products of other similar reactions. In Chapter 5 we described typical reactions of hydrogen, oxygen, and their compounds. These reactions illustrate periodic relationships with respect to chemical properties. It should be emphasized that our system is not an attempt to transform nature so that it fits into small categories but rather an effort to give some order to our many observations of chemical reactions.

6-5 Oxidation–Reduction Reactions: Introduction

The term “oxidation” originally referred to the combination of a substance with oxygen. This results in an increase in the oxidation state of an element in that substance. According to the original definition, the following reactions involve oxidation of the substance shown on the far left of each equation. Oxidation states are shown for *one* atom of the indicated kind.



Originally, *reduction* described the removal of oxygen from a compound. Oxide ores are reduced to metals (a very real reduction in mass). For example, tungsten for use in light bulb filaments can be prepared by reduction of tungsten(VI) oxide with hydrogen at 1200°C:



Tungsten is reduced, and its oxidation state decreases from +6 to zero. Hydrogen is oxidized from zero to the +1 oxidation state. The terms “oxidation” and “reduction” are now applied much more broadly.

Oxidation is an increase in oxidation state and corresponds to the loss, or apparent loss, of electrons. **Reduction** is a decrease in oxidation state and corresponds to a gain, or apparent gain, of electrons.

Electrons are neither created nor destroyed in chemical reactions. So oxidation and reduction always occur simultaneously, and to the same extent, in ordinary chemical reactions. In the four equations cited previously as *examples of oxidation*, the oxidation states of iron and carbon atoms increase as they are oxidized. In each case oxygen is reduced as its oxidation state decreases from zero to –2.

Because oxidation and reduction occur simultaneously in all of these reactions, they are referred to as **oxidation–reduction reactions**. For brevity, we usually call them **redox reactions**. Redox reactions occur in nearly every area of chemistry and biochemistry. We need to be able to identify oxidizing agents and reducing agents and to balance

► Oxidation state is a formal concept adopted for our convenience. The numbers are determined by relying on rules. These rules can result in a fractional oxidation state, as shown here. This does not mean that electronic charges are split.

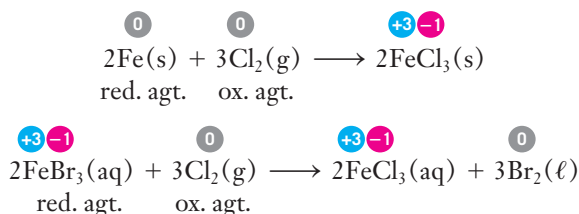
► The terms “oxidation number” and “oxidation state” are often used interchangeably.

► In biological systems, *reduction* often corresponds to the addition of hydrogen to molecules or polyatomic ions and *oxidation* often corresponds to the removal of hydrogen.

oxidation–reduction equations. These skills are necessary for the study of electrochemistry in Chapter 21. Electrochemistry involves electron transfer between physically separated oxidizing and reducing agents and interconversions between chemical energy and electrical energy. These skills are also fundamental to the study of biology, biochemistry, environmental science, and materials science.

Oxidizing agents are species that (1) oxidize other substances, (2) contain atoms that are reduced, and (3) gain (or appear to gain) electrons. **Reducing agents** are species that (1) reduce other substances, (2) contain atoms that are oxidized, and (3) lose (or appear to lose) electrons.

The following equations represent examples of redox reactions. Oxidation states are shown above the formulas, and oxidizing and reducing agents are indicated:



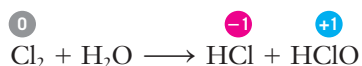
Equations for redox reactions can also be written as total ionic and net ionic equations. For example, the second equation may also be written as:



We distinguish between oxidation states and actual charges on ions by denoting oxidation numbers as $+n$ or $-n$ in circles just above the symbols of the elements, and actual charges as $n+$ or $n-$ above and to the right of formulas of ions. The spectator ions, Fe^{3+} , do not participate in electron transfer. Their cancellation allows us to focus on the oxidizing agent, $\text{Cl}_2(\text{g})$, and the reducing agent, $\text{Br}^{-}(\text{aq})$.



A **disproportionation reaction** is a redox reaction in which the same element is oxidized and reduced. An example is:



STOP & THINK

Oxidation cannot occur without reduction (and vice versa). An **oxidizing agent** in a chemical reaction is *reduced*, while a **reducing agent** is *oxidized*. This can be very confusing, so take some extra time to understand these important relationships.

► The following abbreviations are widely used:

ox. no. = oxidation number
ox. agt. = oxidizing agent
red. agt. = reducing agent



Charles Steele

Iron reacts with chlorine to form iron(III) chloride.

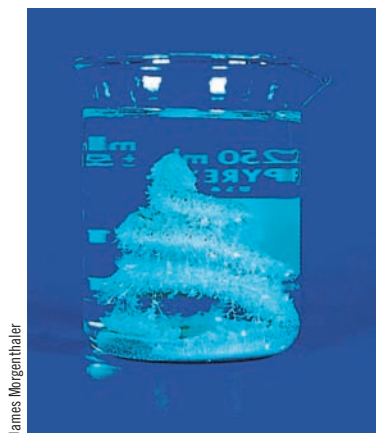
EXAMPLE 6-4 Redox Reactions

Write each of the following formula unit equations as a net ionic equation if the two differ. Which ones are redox reactions? For the redox reactions, identify the oxidizing agent, the reducing agent, the species oxidized, and the species reduced.

- $2\text{AgNO}_3(\text{aq}) + \text{Cu}(\text{s}) \longrightarrow \text{Cu}(\text{NO}_3)_2(\text{aq}) + 2\text{Ag}(\text{s})$
- $4\text{KClO}_3(\text{s}) \xrightarrow{\text{heat}} \text{KCl}(\text{s}) + 3\text{KClO}_4(\text{s})$
- $3\text{AgNO}_3(\text{aq}) + \text{K}_3\text{PO}_4(\text{aq}) \longrightarrow \text{Ag}_3\text{PO}_4(\text{s}) + 3\text{KNO}_3(\text{aq})$

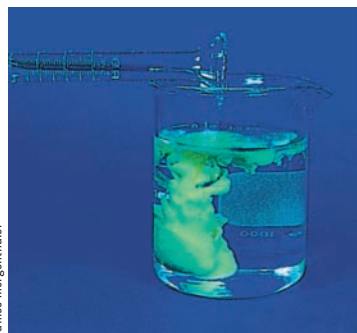
Plan

To write ionic equations, we must recognize compounds that are (1) soluble in water and (2) ionized or dissociated in aqueous solutions. To determine which are oxidation–reduction reactions, we should assign an oxidation state to each element.



James Mortenthaler

Metallic silver formed by immersing a spiral of copper wire in a silver nitrate solution (see Example 6-4a).

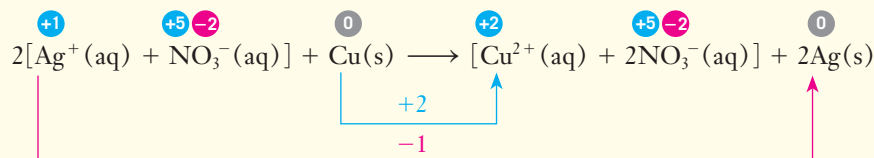


James Mortenthaler

The reaction of $\text{AgNO}_3(\text{aq})$ and $\text{K}_3\text{PO}_4(\text{aq})$ is a precipitation reaction (see Example 6-4c).

Solution

- (a) According to the solubility guidelines (see Section 6-1, Part 5), both silver nitrate, AgNO_3 , and copper(II) nitrate, $\text{Cu}(\text{NO}_3)_2$, are water-soluble ionic compounds. The total ionic equation and oxidation states are:

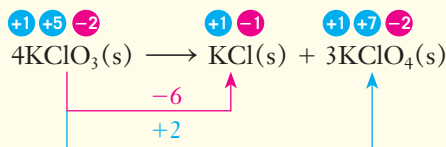


The nitrate ions, NO_3^- , are spectator ions. Canceling them from both sides gives the net ionic equation:



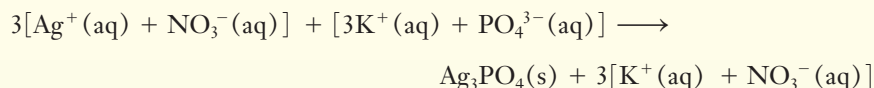
This is a redox equation. The oxidation state of silver decreases from +1 to zero; silver ion is reduced and is the oxidizing agent. The oxidation state of copper increases from zero to +2; copper is oxidized and is the reducing agent.

- (b) This reaction involves only solids, so there are no ions in solution, and the formula unit and net ionic equations are identical. It is a redox reaction:

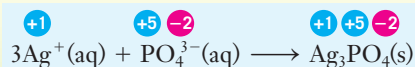


Chlorine is reduced from +5 in KClO_3 to the -1 oxidation state in KCl ; the oxidizing agent is KClO_3 . Chlorine is oxidized from +5 in KClO_3 to the +7 oxidation state in KClO_4 . KClO_3 is also the reducing agent. This is a disproportionation reaction. We see that KClO_3 is both the oxidizing agent and the reducing agent.

- (c) The solubility guidelines indicate that all these salts are soluble except for silver phosphate, Ag_3PO_4 . The total ionic equation is



Eliminating the spectator ions gives the net ionic equation:



There are no changes in oxidation states, so this is not a redox reaction.

You should now work Exercises 56 and 59.

Problem-Solving Tip: A Foolproof Way to Recognize a Redox Reaction

You can always recognize a redox reaction by analyzing oxidation states. First determine the oxidation state of each element wherever it appears in the reaction. If no elements change in oxidation states, the reaction is not an oxidation–reduction reaction. If changes do occur, the reaction is an oxidation–reduction reaction. Remember that oxidation and reduction must always occur together; if some elements increase in oxidation states, then others must decrease.

In Chapter 11 we will learn to balance redox equations and to carry out stoichiometric calculations using the balanced equations.

6-6 Combination Reactions

Reactions in which two or more substances combine to form a single compound are called **combination reactions**.

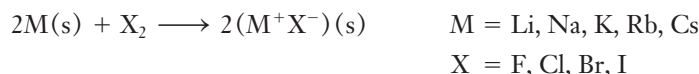
They may involve (1) the combination of two elements to form a compound, (2) the combination of an element and a compound to form a single new compound, or (3) the combination of two compounds to form a single new compound. Let's examine some of these reactions.

1 Element + Element $\longrightarrow$ Compound

For this type of combination reaction, each element goes from an uncombined state, where its oxidation state is zero, to a combined state in a compound, where its oxidation state is not zero. Thus reactions of this type are oxidation–reduction reactions (see Section 6-5).

Metal + Nonmetal $\rightarrow$ Binary Ionic Compound

Most metals (low electronegativity) react with most nonmetals (higher electronegativity) to form binary ionic compounds. The Group 1A metals combine vigorously with the Group 7A nonmetals to form binary *ionic* compounds with the general formula MX (see Section 7-2):



This general equation thus represents the 20 combination reactions that form the ionic compounds listed in Table 6-8. Sodium, a silvery-white metal, combines with chlorine, a pale green gas, to form sodium chloride, or ordinary table salt. All members of both families undergo similar reactions.



As we might expect, the Group 2A metals also combine with the Group 7A nonmetals to form binary compounds. Except for BeCl_2 , BeBr_2 , and BeI_2 , these are ionic compounds. In general terms these combination reactions may be represented as:



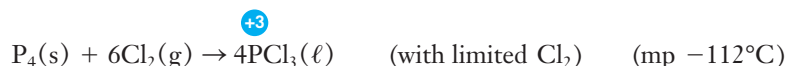
Consider the reaction of magnesium with fluorine to form magnesium fluoride:



Because all the 2A and 7A elements undergo similar reactions, the general equation, written above, represents 20 reactions. We omit radium and astatine, the rare and highly radioactive members of the families.

Nonmetal + Nonmetal $\longrightarrow$ Binary Covalent Compound

When two nonmetals combine with each other, they form binary *covalent* compounds. In such reactions, the oxidation state of the element with the more positive oxidation state is often variable, depending on reaction conditions. For example, phosphorus (Group 5A) combines with a *limited amount* of chlorine to form phosphorus trichloride, in which phosphorus exhibits the +3 oxidation state.



Charles D. Winters

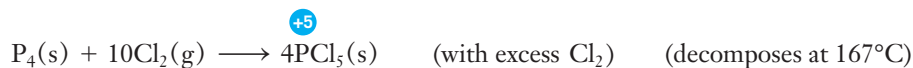
Potassium, a metal, reacts with chlorine, a nonmetal, to form potassium chloride, KCl. The reaction releases energy in the form of heat and light.

► Another important reaction of this kind is the formation of metal oxides (see Section 5-9).

Table 6-8 Alkali Metal Halides: Compounds Formed by Group 1A and 7A Elements

LiF	LiCl	LiBr	LiI
NaF	NaCl	NaBr	NaI
KF	KCl	KBr	KI
RbF	RbCl	RbBr	RbI
CsF	CsCl	CsBr	CsI

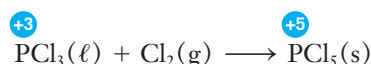
With an excess of chlorine, the product is phosphorus pentachloride, which contains phosphorus in the +5 oxidation state:



In general, *a higher oxidation state of a nonmetal is formed when it reacts with an excess of another more electronegative nonmetal*. There are many more reactions in which two elements combine to form a compound (see Sections 5-8 and 5-9).

2 Compound + Element $\longrightarrow$ Compound

Phosphorus in the +3 oxidation state in PCl_3 molecules can be converted to the +5 state in PCl_5 by combination with chlorine:



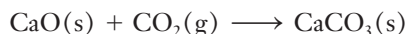
Likewise, sulfur in the +4 state is converted to the +6 state when SF_4 reacts with fluorine to form SF_6 :



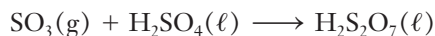
Combination reactions of this type are also oxidation–reduction reactions.

3 Compound + Compound $\longrightarrow$ Compound

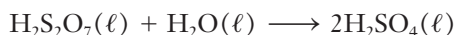
An example of reactions in this category is the combination of calcium oxide with carbon dioxide to produce calcium carbonate:



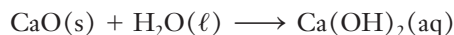
Pyrosulfuric acid is produced by dissolving sulfur trioxide in concentrated sulfuric acid:



Pyrosulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$, is then diluted with water to make H_2SO_4 :



Oxides of the Group 1A and 2A metals react with water to form metal hydroxides, e.g.:



6-7 Decomposition Reactions

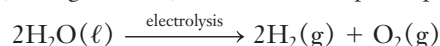
► Decomposition reactions can be considered as the opposite of combination reactions. A decomposition reaction may or may not also be an oxidation–reduction reaction. You can always identify a redox reaction by determining the oxidation state of each element in each occurrence in the reaction (see the Problem-Solving Tip in Section 6-5).

Decomposition reactions are those in which a compound decomposes to produce (1) two elements, (2) one or more elements *and* one or more compounds, or (3) two or more compounds.

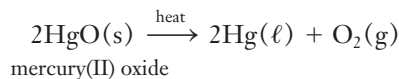
Examples of each type follow.

1 Compound $\longrightarrow$ Element + Element

The electrolysis of water produces two elements by the decomposition of a compound. A compound that ionizes, such as H_2SO_4 , is added to increase the conductivity of water and the rate of the reaction (see Figure 1-13), but it does not participate in the reaction:

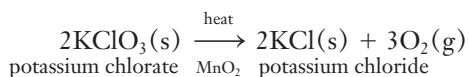


Small amounts of oxygen can be prepared by the thermal decomposition of certain oxygen-containing compounds. Some metal oxides, such as mercury(II) oxide, HgO , decompose on heating to produce oxygen:



2 Compound $\longrightarrow$ Compound + Element

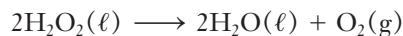
The alkali metal chlorates, such as KClO_3 , decompose when heated to produce the corresponding chlorides and liberate oxygen. Potassium chlorate is a common laboratory source for small amounts of oxygen:



Nitrate salts of alkali metals or alkaline earth metals decompose to form metal nitrites and oxygen gas.

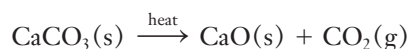


Hydrogen peroxide decomposes to form water and oxygen even at room temperature. H_2O_2 is usually stored in a refrigerator to slow down this decomposition reaction.



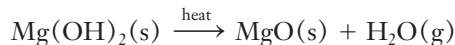
3 Compound $\longrightarrow$ Compound + Compound

The thermal decomposition of calcium carbonate (limestone) and other carbonates produces two compounds, a metal oxide and carbon dioxide:



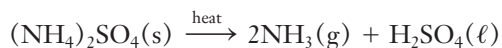
This is an important reaction in the production of cement. Calcium oxide (commonly called lime) is also used as a base in industrial processes.

When some solid hydroxides are heated, they decompose to form a metal oxide and water vapor.

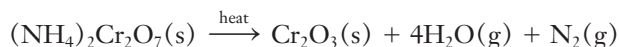


Magnesium oxide, MgO , is pressed into sheets for use as a thermal insulating material in oven walls.

Ammonium salts lose ammonia.

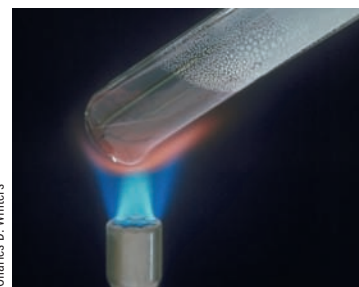


If the ammonium salt contains an anion that is a strong oxidizing agent (e.g., nitrate, nitrite, or dichromate), its decomposition reaction produces an oxide, water (as vapor at high temperatures), and nitrogen gas. Such a reaction is a redox reaction.



6-8 Displacement Reactions

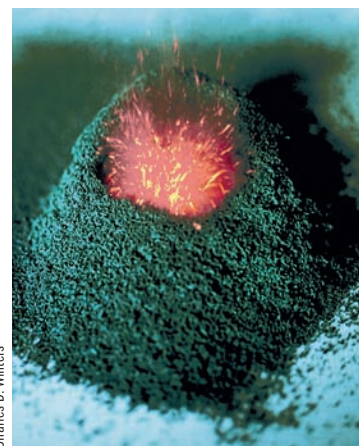
Reactions in which one element displaces another from a compound are called **displacement reactions**.



Charles D. Winters

Mercury(II) oxide, a red compound, decomposes when heated into the two elements: mercury (a metal) and oxygen (a nonmetal).

► Manganese dioxide, MnO_2 , is used as a catalyst, a substance that speeds up a chemical reaction but is not consumed. Here it allows the decomposition to occur at a lower temperature.



Charles D. Winters

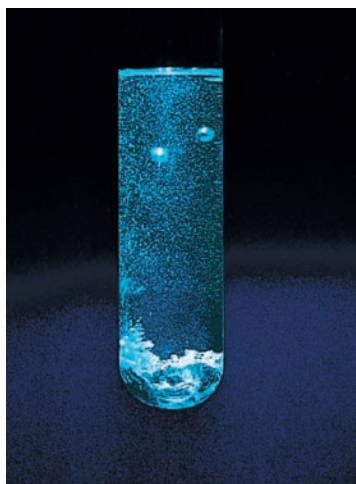
Solid ammonium dichromate, $[(\text{NH}_4)_2\text{Cr}_2\text{O}_7]$, orange decomposes when heated into chromium(III) oxide, (Cr_2O_3) , green, nitrogen, and steam (water vapor). This reaction is sometimes demonstrated as the “classroom volcano,” but it must be done with extreme caution due to the carcinogenic (cancer-causing) nature of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

Unless otherwise noted, all content on this page is © Cengage Learning.



James Morgenstern

A strip of zinc metal was placed in a blue solution of copper(II) sulfate, CuSO_4 . The copper has been displaced from solution and has fallen to the bottom of the beaker. The resulting zinc sulfate, ZnSO_4 , solution is colorless.



Charles Steele

Zinc reacts with dilute H_2SO_4 to produce H_2 and a solution that contains ZnSO_4 . This is a displacement reaction.

These reactions are always redox reactions. The lower the electronegativity of a metal, the more readily that metal undergoes oxidation, and the more active we say it is.

More active (less electronegative) metals displace less active (more electronegative) metals or hydrogen from their compounds in aqueous solution to form the oxidized form of the more active metal and the reduced (free metal) form of the other metal or hydrogen gas.

In Table 6-9, the most active metals are listed at the top of the first column. These metals tend to react to form their oxidized forms (cations). Elements at the bottom of the activity series (the first column of Table 6-9) are the most electronegative and tend to remain in their reduced form. They are easily converted from their oxidized forms to their reduced forms.



The reaction of copper with silver nitrate that was described in detail in Section 6-2 is typical. Please refer to it.

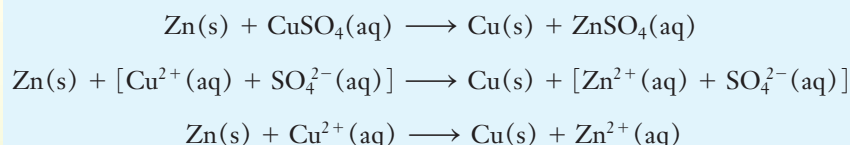
EXAMPLE 6-5 Displacement Reaction

A large piece of zinc metal is placed in a copper(II) sulfate, CuSO_4 , solution. The blue solution becomes colorless as finely divided copper metal falls to the bottom of the container. The resulting solution contains zinc sulfate, ZnSO_4 . Write balanced formula unit, total ionic, and net ionic equations for the reaction.

Plan

The metals zinc and copper are *not* ionized or dissociated in contact with H_2O . Both CuSO_4 and ZnSO_4 are soluble salts (solubility guideline 5), so they are written in ionic form.

Solution

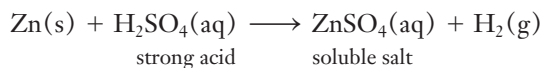


In this *displacement reaction*, the more active metal, zinc, displaces the ions of the less active metal, copper, from aqueous solution.

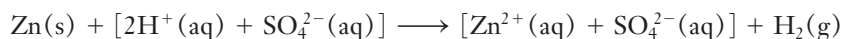
You should now work Exercise 64.

2 [Active Metal + Nonoxidizing Acid] $\longrightarrow$ [Hydrogen + Salt of Acid]

A common method for preparing small amounts of hydrogen involves the reaction of active metals with nonoxidizing acids, such as HCl and H_2SO_4 . For example, when zinc is dissolved in H_2SO_4 , the reaction produces zinc sulfate; hydrogen is displaced from the acid, and it bubbles off as gaseous H_2 . The formula unit equation for this reaction is



Both sulfuric acid (in very dilute solution) and zinc sulfate exist primarily as ions, so the total ionic equation is



Elimination of spectator ions from the total ionic equation gives the net ionic equation:



Table 6-9 Activity Series of Some Elements

Element			Common Reduced Form	Common Oxidized Forms
Li	Displace hydrogen from nonoxidizing acids	Displace hydrogen from cold water	Li	Li ⁺
K			K	K ⁺
Ca			Ca	Ca ²⁺
Na		Displace hydrogen from steam	Na	Na ⁺
Mg			Mg	Mg ²⁺
Al			Al	Al ³⁺
Mn			Mn	Mn ²⁺
Zn			Zn	Zn ²⁺
Cr			Cr	Cr ³⁺ , Cr ⁶⁺
Fe			Fe	Fe ²⁺ , Fe ³⁺
Cd		Cd	Cd ²⁺	
Co		Co	Co ²⁺	
Ni		Ni	Ni ²⁺	
Sn		Sn	Sn ²⁺ , Sn ⁴⁺	
Pb		Pb	Pb ²⁺ , Pb ⁴⁺	
H (a nonmetal)		H ₂	H ⁺	
Sb (a metalloid)		Sb	Sb ³⁺	
Cu		Cu	Cu ⁺ , Cu ²⁺	
Hg		Hg	Hg ₂ ²⁺ , Hg ²⁺	
Ag		Ag	Ag ⁺	
Pt	Pt	Pt ²⁺ , Pt ⁴⁺		
Au		Au	Au ⁺ , Au ³⁺	

Increasing Activity
(Oxidized Form Favored)

Increasing Activity
(Oxidized Form Favored)

Table 6-9 lists the **activity series**. When any metal listed above hydrogen in this series is added to a solution of a *nonoxidizing* acid such as hydrochloric acid, HCl, or sulfuric acid, H₂SO₄, the metal dissolves to produce hydrogen, and a salt is formed. HNO₃ is the common *oxidizing acid*. It reacts with active metals to produce oxides of nitrogen, but *not* hydrogen, H₂.

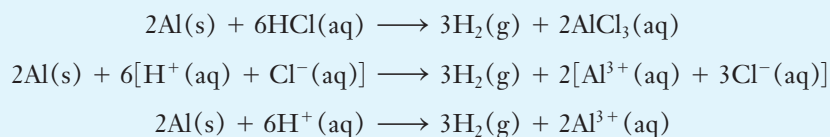
EXAMPLE 6-6 Displacement Reaction

Which of the following metals can displace hydrogen from hydrochloric acid solution? Write balanced formula unit, total ionic, and net ionic equations for reactions that can occur.

Al, Cu, Ag

Plan

The activity series of the metals, Table 6-9, tells us that copper and silver *do not* displace hydrogen from solutions of nonoxidizing acids. Aluminum is an active metal that can displace H₂ from HCl and form aluminum chloride.

Solution

You should now work Exercise 63.



Charles Steele

Aluminum displaces H₂ from a hydrochloric acid solution.

Unless otherwise noted, all content on this page is © Cengage Learning.

CHEMISTRY IN USE

Troublesome Displacement Reactions

The deterioration of the Statue of Liberty and the damage done at the Three Mile Island and Chernobyl nuclear facilities are just a few of the major problems that have resulted from ignorance about chemical reactivity.

When originally constructed over one hundred years ago the Statue of Liberty had a 200,000-pound outer copper skin supported by a framework of 2000 iron bars. First, oxygen in the air oxidized the copper skin to form copper oxide. In a series of reactions, iron (the more active metal) then reduced the Cu^{2+} ions in copper oxide.



Over the years, the supporting iron frame was reduced to less than half its original thickness; this made necessary the repairs done to the statue before the celebration of its 100th birthday on July 4, 1986.

Two major nuclear power plant accidents, one at Three Mile Island near Harrisburg, Pennsylvania, in 1979 and the other at Chernobyl in Ukraine in 1986, were also unexpected consequences of chemical reactivity. In each case, cooling pump failures sent temperatures soaring above 340°C . Like aluminum, zirconium (used in building the reactors) forms an oxide coating that shields it from further reactions. However, that protective coating breaks down at high temperatures. Without its protective coating, zirconium reacts with steam.



At Three Mile Island, this displacement reaction produced a 1000-cubic foot bubble of hydrogen gas. Because hydrogen is easily ignited by a spark, the nuclear power plant was in real danger of a complete meltdown until the hydrogen could be removed.

During the Middle Ages (~AD 400–1400), another displacement reaction completely misled alchemists into foolishly pursuing a philosophers' stone that was believed to have the power to turn base metals such as iron and lead into more precious metals such as silver and gold. The alchemists' ignorance of relative activities of metals led them to believe that they had turned iron into a more precious metal when they inserted an iron rod into a blue copper(II) sulfate solution. In fact, the following displacement reaction had occurred, plating shiny copper metal onto the iron rod:



In the 1960s and 1970s, some automobile manufacturers showed their ignorance of chemical reactivity by building cars with aluminum water pumps and aluminum engine heads attached to cast-iron engine blocks. These water pumps often



leaked and the engine heads quickly deteriorated. These problems occurred as the more active aluminum reacted with iron(III) oxide (formed when the iron engine reacted with atmospheric oxygen).



Some dentists have made similar mistakes by placing gold caps over teeth that are adjacent to existing fillings. The slightly oxidized gold can react with a dental amalgam filling (an alloy of silver, tin, copper, and mercury). As the dental amalgam is oxidized, it dissolves in saliva to produce a persistent metallic taste in the patient's mouth.

When plumbers connect galvanized pipes (iron pipes coated with zinc) to copper pipes, copper ions oxidize the zinc coating and expose the underlying iron, allowing it to rust. The displacement reaction that occurs is



Once the zinc coating has been punctured on an iron pipe, oxidation of the iron pipes occurs rapidly because iron is a more active metal than copper.

It is important to keep in mind that a variety of reactions other than the displacement reactions discussed here probably take place. For example, less active metals (such as copper) can conduct electrons from the metals being oxidized to oxidizing agents (such as oxygen or the oxide of nitrogen and sulfur) that are present in the atmosphere. Oxygen plays an important role in all these displacement examples.

RONALD DELORENZO
MIDDLE GEORGIA COLLEGE

Very active metals can even displace hydrogen from water. The reaction of potassium, or another metal of Group 1A, with water is also a *displacement reaction*:



Such reactions of very active metals of Group 1A are dangerous, however, because they generate enough heat to cause explosive ignition of the hydrogen.

EXAMPLE 6-7 Displacement Reaction

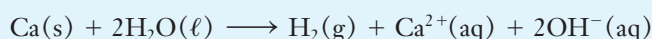
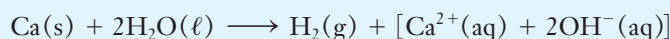
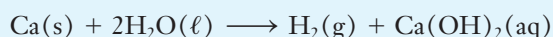
Which of the following metals can displace hydrogen from water at room temperature? Write balanced formula unit, total ionic, and net ionic equations for reactions that can occur.



Plan

The activity series, Table 6-9, tells us that tin and mercury *cannot* displace hydrogen from water. Calcium is a very active metal (see Table 6-9) that displaces hydrogen from cold water (Figure 6-3) and forms calcium hydroxide, a strong base.

Solution



You should now work Exercise 71.

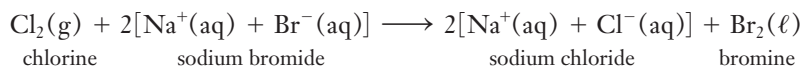


Charles D. Winters

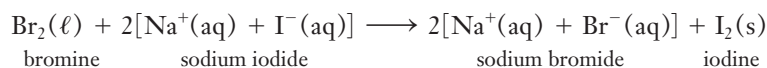
Figure 6-3 The displacement reaction of calcium with water at room temperature produces bubbles of hydrogen.



Many *nonmetals* displace less active nonmetals from combination with a metal or other cation. For example, when chlorine is bubbled through a solution containing bromide ions (derived from a soluble salt such as sodium bromide, NaBr), chlorine displaces bromide ions to form elemental bromine and chloride ions (as aqueous sodium chloride):



Similarly, when bromine is added to a solution containing iodide ions, the iodide ions are displaced by bromine to form iodine and bromide ions:



Each halogen will displace less active (less electronegative) halogens from their binary salts; that is, the order of decreasing activities is



Conversely, a halogen will *not* displace more active (more electronegative) members from their salts:



EXAMPLE 6-8 Displacement Reaction

Which of the following combinations would result in a displacement reaction? Write balanced formula unit, total ionic, and net ionic equations for reactions that occur.

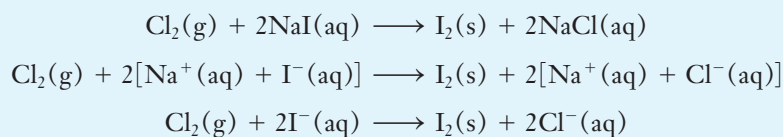
- (a) $\text{I}_2(\text{s}) + \text{NaBr}(\text{aq}) \longrightarrow$
 (b) $\text{Cl}_2(\text{g}) + \text{NaI}(\text{aq}) \longrightarrow$
 (c) $\text{Br}_2(\ell) + \text{NaCl}(\text{aq}) \longrightarrow$

Plan

The activity of the halogens decreases as their electronegativity decreases from top to bottom in the periodic table. We see (a) that Br is above I and (c) that Cl is above Br in the periodic table; therefore, neither combination (a) nor combination (c) could result in reaction. Cl is above I in the periodic table, and so combination (b) results in a displacement reaction.

Solution

The more active halogen, Cl_2 , displaces the less active halogen, I_2 , from its compounds.



You should now work Exercise 72.

► Activity of the halogens decreases going down the group in the periodic table.



Charles D. Winters

A Bromine, Br_2 , in water (pale orange) is poured into an aqueous solution of NaI , the top layer in the cylinder.

A nonmetal-nonmetal displacement reaction.



B Br_2 displaces I^- from solution and forms solid iodine, I_2 . The I_2 dissolves in water to give a brown solution but is more soluble in many organic liquids (purple bottom layer).

6-9 Metathesis Reactions

In many reactions between two compounds in aqueous solution, the positive and negative ions appear to “change partners” to form two new compounds, with *no change in oxidation numbers*. Such reactions are called **metathesis reactions**.

We can represent such reactions by the following general equation, where A and B represent positive ions (cations) and X and Y represent negative ions (anions):



For example, when we mix silver nitrate and sodium chloride solutions, solid silver chloride is formed and sodium nitrate remains dissolved in water:



Metathesis reactions result in the removal of ions from solution; this removal of ions can be thought of as the *driving force* for the reaction—the reason it occurs. The removal of ions can occur in various ways, which can be used to classify types of metathesis reactions:

1. Formation of predominantly nonionized molecules (weak or nonelectrolytes) in solution; the most common such nonelectrolyte product is water
2. Formation of an insoluble solid, called a precipitate (which separates from the solution)

► Pronounced “meh-tath-uh-sis.” Metathesis reactions are sometimes referred to as **double displacement reactions**.

1 Acid–Base (Neutralization) Reactions: Formation of a Nonelectrolyte

Acid–base reactions are among the most important kinds of chemical reactions. Many acid–base reactions occur in nature in both plants and animals. Many acids and bases are essential compounds in an industrialized society (Table 6-10). For example, approximately 300 pounds of sulfuric acid, H_2SO_4 , and approximately 100 pounds of ammonia, NH_3 , are required to support the lifestyle of an average American for one year.

The reaction of an acid with a metal hydroxide base produces a salt and water. Such reactions are called **neutralization reactions** because the typical properties of acids and bases are neutralized.

In nearly all neutralization reactions, the driving force is the combination of $\text{H}^+(\text{aq})$ from an acid and $\text{OH}^-(\text{aq})$ from a base (or a base plus water) to form water molecules.

Consider the reaction of hydrochloric acid, $\text{HCl}(\text{aq})$, with aqueous sodium hydroxide, NaOH . Table 6-1 tells us that HCl is a strong acid, and Table 6-3 tells us that NaOH is a

► The manufacture of fertilizers consumes more H_2SO_4 and more NH_3 than any other single use.

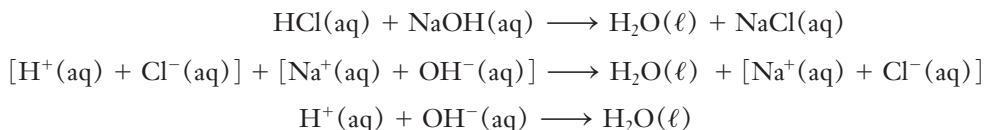
► When a base such as ammonia or an amine reacts with an acid, a salt, but no water, is formed. This is still called an acid–base, or neutralization, reaction.

Table 6-10 2009 Production of Inorganic Acids, Bases, and Salts in the United States

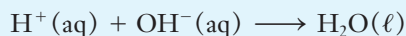
Formula	Name	Billions of Pounds	Major Uses
H_2SO_4	sulfuric acid	64.25	Manufacture of fertilizers and other chemicals
CaO , $\text{Ca}(\text{OH})_2$	lime (calcium oxide and calcium hydroxide)	40.67	Manufacture of other chemicals, steelmaking, water treatment
Na_2CO_3	sodium carbonate (soda ash)	20.91	Manufacture of glass, other chemicals, detergents, pulp, and paper
NH_3	ammonia	20.66	Fertilizer; manufacture of fertilizers and other chemicals
H_3PO_4	phosphoric acid	19.08	Manufacture of fertilizers
NaOH	sodium hydroxide	14.48	Manufacture of other chemicals, pulp and paper, soap and detergents, aluminum, textiles
NH_4NO_3	ammonium nitrate	13.88	Fertilizer and explosives
HNO_3	nitric acid	13.06	Manufacture of fertilizers, explosives, plastics, and lacquers
HCl	hydrochloric acid	7.16	Manufacture of other chemicals and rubber; metal cleaning
$(\text{NH}_4)_2\text{SO}_4$	ammonium sulfate	5.00	Fertilizer
KOH , K_2CO_3	potash	2.25	Manufacture of fertilizers
$\text{Al}_2(\text{SO}_4)_3$	aluminum sulfate	1.66	Water treatment, dyeing textiles
NaClO_3	sodium chlorate	1.04	Manufacture of other chemicals, explosives, plastics
Na_2SO_4	sodium sulfate	0.83	Manufacture of paper, glass, and detergents

Unless otherwise noted, all content on this page is © Cengage Learning.

strong base. The salt sodium chloride, NaCl, is formed in this reaction. It contains the cation of its parent base, Na⁺, and the anion of its parent acid, Cl⁻. Solubility guidelines 2 and 4 (see page 213) tell us that NaCl is a soluble salt.



The net ionic equation for *all* reactions of strong acids with strong bases that form soluble salts and water is



Problem-Solving Tip Salt Formation

The salt that is formed in a neutralization reaction is composed of the cation of the base and the anion of the acid. The salt may be soluble or insoluble. If our goal were to obtain the salt from the reaction of aqueous HCl with aqueous NaOH, we could evaporate the water and obtain solid NaCl.

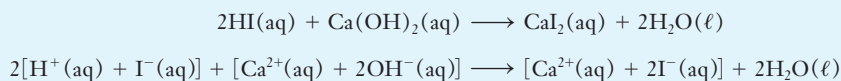
EXAMPLE 6-9 Neutralization Reactions

Predict the products of the reaction between HI(aq) and Ca(OH)₂(aq). Write balanced formula unit, total ionic, and net ionic equations.

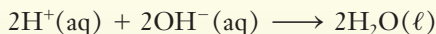
Plan

This is an acid–base neutralization reaction; the products are H₂O and the salt that contains the cation of the base, Ca²⁺, and the anion of the acid, I⁻; CaI₂ is a soluble salt (solubility guideline 4). HI is a strong acid (see Table 6-1), Ca(OH)₂ is a strong base (see Table 6-3), and CaI₂ is a soluble salt, so all are written in ionic form.

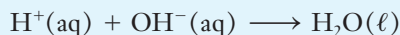
Solution



We cancel the spectator ions.



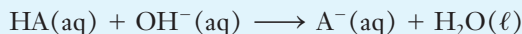
Dividing by 2 gives the net ionic equation:



You should now work Exercise 77.

Reactions of *weak* acids with strong bases also produce salts and water, but there is a significant difference in the balanced ionic equations because weak acids are only *slightly* ionized.

The reactions of *weak monoprotic acids* with *strong bases* that form *soluble salts* can be represented in general terms as



where HA represents the weak acid and A⁻ represents its anion.

► Recall that in balanced equations we show the smallest whole-number coefficients possible.

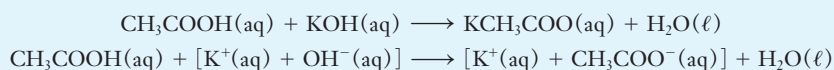
► A *monoprotic acid* contains one acidic H per formula unit.

EXAMPLE 6-10 Neutralization Reactions

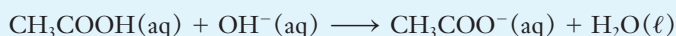
Write balanced formula unit, total ionic, and net ionic equations for the reaction of acetic acid with potassium hydroxide.

Plan

Neutralization reactions involving metal hydroxide bases produce a salt and water. CH_3COOH is a weak acid (see Table 6-2), so it is written as formula units. KOH is a strong base (see Table 6-3) and KCH_3COO is a soluble salt (solubility guidelines 2 and 3), so both are written in ionic form.

Solution

The spectator ion is K^+ , the cation of the strong base, KOH .



Thus, we see that *this* net ionic equation includes *molecules* of the weak acid and *anions* of the weak acid.

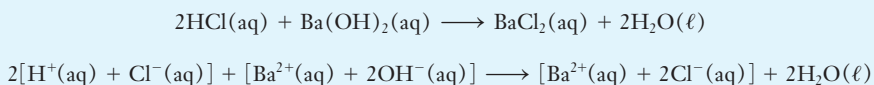
You should now work Exercise 78.

EXAMPLE 6-11 Salt Formation

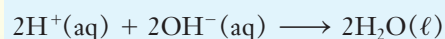
Write balanced formula unit, total ionic, and net ionic equations for an acid–base reaction that will produce the salt, barium chloride.

Plan

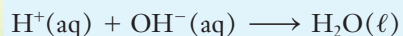
Neutralization reactions produce a salt. The salt contains the cation from the base and the anion from the acid. The base must therefore contain Ba^{2+} , that is, $\text{Ba}(\text{OH})_2$, and the acid must contain Cl^- , that is, HCl . We write equations that represent the reaction between the strong base, $\text{Ba}(\text{OH})_2$, and the strong acid, HCl .

Solution

We cancel the spectator ions.



Dividing by 2 gives the net ionic equation:



You should now work Exercise 86.

► The net ionic equation shows the driving force for this reaction. The formula unit equation shows the salt formed or that could be isolated if the water were evaporated.

2 Precipitation Reactions

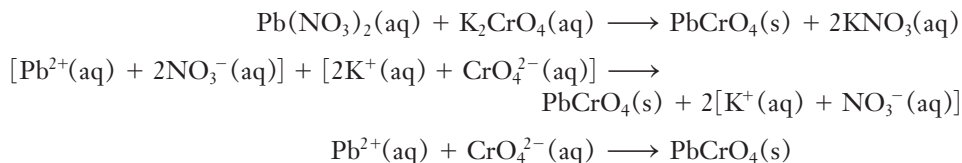
In **precipitation reactions** an insoluble solid, a **precipitate**, forms and then settles out of solution. The driving force for these reactions is the strong attraction between cations and anions. This results in the removal of ions from solution by the formation of a precipitate. Our teeth and bones were formed by very slow precipitation reactions in which mostly calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ was deposited in the correct geometric arrangements.

► To understand the discussion of precipitation reactions, you must know the solubility guidelines, Table 6-4.

Unless otherwise noted, all content on this page is © Cengage Learning.

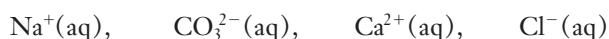
An example of a precipitation reaction is the formation of bright yellow insoluble lead(II) chromate when we mix solutions of the soluble ionic compounds lead(II) nitrate and potassium chromate (Figure 6-4). The other product of the reaction is KNO_3 , a soluble salt.

The balanced formula unit, total ionic, and net ionic equations for this reaction follow:



Another important precipitation reaction involves the formation of insoluble carbonates (solubility guideline 7). Limestone deposits are mostly calcium carbonate, CaCO_3 , although many also contain significant amounts of magnesium carbonate, MgCO_3 .

Suppose we mix together aqueous solutions of sodium carbonate, Na_2CO_3 , and calcium chloride, CaCl_2 . We recognize that *both* Na_2CO_3 and CaCl_2 (solubility guidelines 2, 4a, and 7) are soluble ionic compounds. At the instant of mixing, the resulting solution contains four ions:



One pair of ions, Na^{+} and Cl^{-} , *cannot* form an insoluble compound (solubility guidelines 2 and 4). We look for a pair of ions that could form an insoluble compound. Ca^{2+} ions and CO_3^{2-} ions are such a combination; they form insoluble CaCO_3 (solubility guideline 7). The equations for the reaction follow:

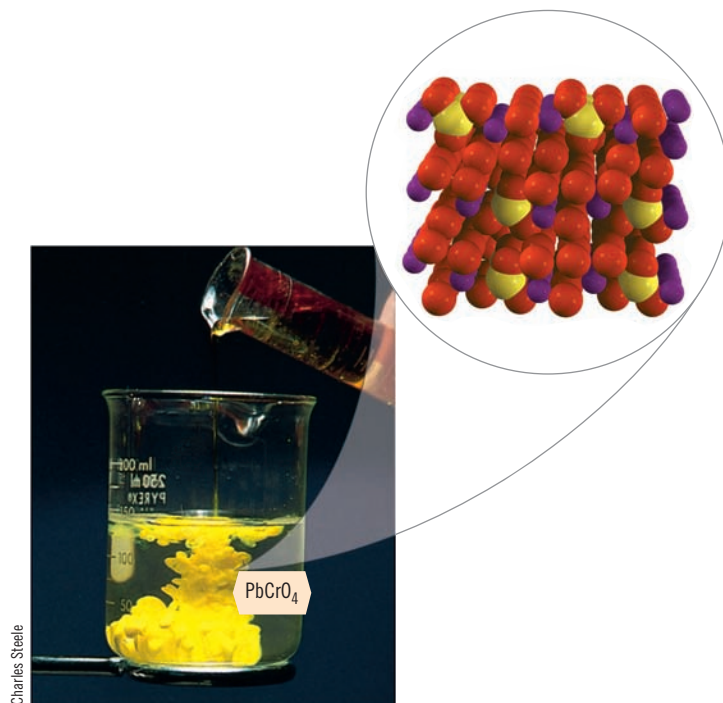
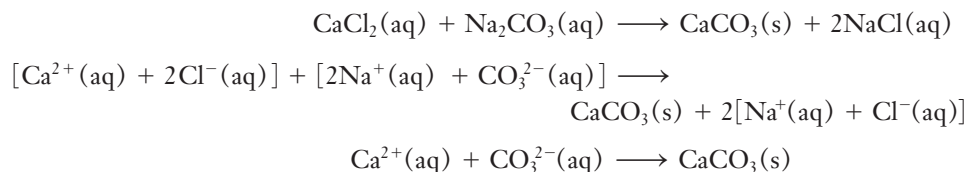


Figure 6-4 A precipitation reaction. When K_2CrO_4 solution is added to aqueous $\text{Pb}(\text{NO}_3)_2$ solution, the yellow compound PbCrO_4 precipitates. The resulting solution contains K^{+} and NO_3^{-} ions, the ions of KNO_3 .

EXAMPLE 6-12 Solubility Guidelines and Precipitation Reactions

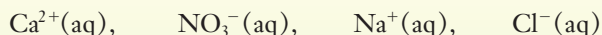
Will a precipitate form when aqueous solutions of $\text{Ca}(\text{NO}_3)_2$ and NaCl are mixed in reasonable concentrations? Write balanced formula unit, total ionic, and net ionic equations for any reaction.

Plan

We recognize that both $\text{Ca}(\text{NO}_3)_2$ (solubility guideline 3) and NaCl (solubility guidelines 2 and 4) are soluble compounds. We use the solubility guidelines to determine whether any of the possible products are insoluble.

Solution

At the instant of mixing, the resulting solution contains four ions:



New combinations of ions *could* be CaCl_2 and NaNO_3 . But solubility guideline 4 tells us that CaCl_2 is a soluble compound, and solubility guidelines 2 and 3 tell us that NaNO_3 is a soluble compound. Therefore, no precipitate forms in this solution.

You should now work Exercise 90.



Charles D. Winters

Seashells, which are formed in very slow precipitation reactions, are mostly calcium carbonate (CaCO_3) a white compound. Traces of transition metal ions give them color.

EXAMPLE 6-13 Solubility Guidelines and Precipitation Reactions

Will a precipitate form when aqueous solutions of CaCl_2 and K_3PO_4 are mixed in reasonable concentrations? Write balanced formula unit, total ionic, and net ionic equations for any reaction.

Plan

We recognize that both CaCl_2 (solubility guideline 4) and K_3PO_4 (solubility guideline 2) are soluble compounds. We use the solubility guidelines to determine whether any of the possible products are insoluble.

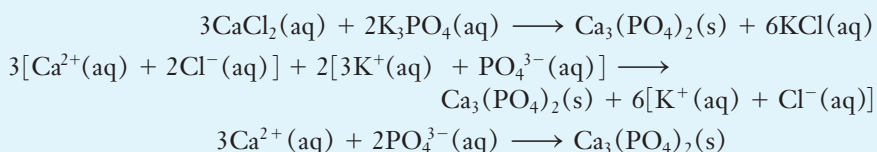
Solution

At the instant of mixing, the resulting solution contains four ions:



New combinations of ions *could* be KCl and $\text{Ca}_3(\text{PO}_4)_2$. Solubility guidelines 2 and 4 tell us that KCl is a soluble compound; solubility guideline 7 tells us that $\text{Ca}_3(\text{PO}_4)_2$ is an insoluble compound, so a precipitate of $\text{Ca}_3(\text{PO}_4)_2$ forms in this solution.

The equations for the formation of calcium phosphate follow:



You should now work Exercise 96.

6-10 Gas-Formation Reactions

When there are *no gaseous reactants*, the formation of an insoluble or slightly soluble gas provides a driving force for a type of reaction that we call a **gas-formation reaction**. The only common gases that are very soluble in water are $\text{HCl}(\text{g})$ and $\text{NH}_3(\text{g})$. The low solubility of other gases can force a reaction to proceed if they are formed as a reaction product.

When an acid—for example, hydrochloric acid—is added to solid calcium carbonate, a reaction occurs in which carbonic acid, a weak acid, is produced.



Charles D. Winters

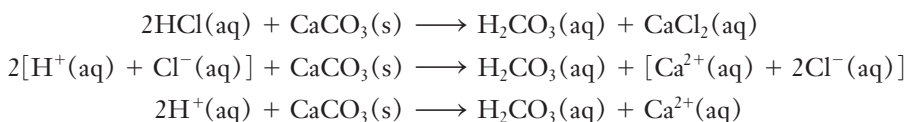
A gas-formation causes muffins or biscuits to rise. When the sodium bicarbonate, NaHCO_3 , in baking powder reacts with an acid, carbon dioxide gas is formed. Baking powders contain acidic salts such as CaHPO_4 or weak organic acids such as tartaric acid, $\text{C}_2\text{H}_2(\text{OH})_2(\text{COOH})_2$.

► Hydrogen sulfide, H_2S , is responsible for the smell of rotten eggs. This gas-formation reaction is also a metathesis reaction.



Charles D. Winters

Blackboard chalk is mostly calcium carbonate, CaCO_3 . Bubbles of carbon dioxide, CO_2 , are clearly visible in this photograph of CaCO_3 reacting with HCl in a gas-forming metathesis reaction.



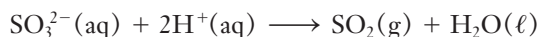
The heat generated in the reaction causes thermal decomposition of carbonic acid to gaseous carbon dioxide and water:



Most of the CO_2 bubbles off, and the reaction goes to completion (with respect to the limiting reactant). The net effect is the conversion of ionic species into nonionized molecules of a gas (CO_2) and water.



Salts containing the sulfite ion, SO_3^{2-} , react with acids in a similar manner to form sulfur dioxide gas, $\text{SO}_2(\text{g})$.



Many sulfide salts react with acids to form gaseous hydrogen sulfide, H_2S . The low solubility of H_2S in water helps the reaction to proceed.



Displacement reactions in which an active metal displaces hydrogen from an acid or from water (see Section 6-8, Part 2) are gas-formation reactions, but they are *not* metathesis reactions.

6-11 Summary of Reaction Types

Table 6-11 summarizes the reaction types we have presented. Remember that a reaction might be classified in more than one category.

EXAMPLE 6-14 Classifying Reactions

Classify each of the following reactions.

- $\text{Zn}(\text{s}) + 2\text{AgNO}_3(\text{aq}) \longrightarrow \text{Zn}(\text{NO}_3)_2(\text{aq}) + 2\text{Ag}(\text{s})$
- $\text{Ca}(\text{OH})_2(\text{s}) \xrightarrow{\text{heat}} \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{g})$
- $2\text{HI}(\text{g}) \xrightarrow{\text{heat}} \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
- $\text{Cu}(\text{NO}_3)_2(\text{aq}) + \text{Na}_2\text{S}(\text{aq}) \longrightarrow \text{CuS}(\text{s}) + 2\text{NaNO}_3(\text{aq})$
- $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\ell) \longrightarrow \text{H}_2\text{SO}_3(\text{aq})$
- $\text{H}_2\text{SO}_3(\text{aq}) + 2\text{KOH}(\text{aq}) \longrightarrow \text{K}_2\text{SO}_3(\text{aq}) + 2\text{H}_2\text{O}(\ell)$

Plan

We identify each reaction type by its characteristics, using Table 6-11 and the appropriate sections as a guide.

Solution

- One element, Zn, displaces another, Ag, from a compound; this is a displacement reaction. Zn is oxidized and Ag is reduced. So this is also an oxidation–reduction (redox) reaction.
- A single compound breaks apart into two compounds; this is a decomposition reaction.
- A single compound breaks apart into two elements; this is another decomposition reaction. However, now there are changes in oxidation numbers; H changes from +1 in HI to 0 in H_2 , and I changes from -1 in HI to 0 in I_2 . So this is also an oxidation–reduction (redox) reaction.
- The positive and negative ions in the two reactant compounds change partners; this is a metathesis reaction. An insoluble product, $\text{CuS}(\text{s})$, is formed, so the reaction is a precipitation reaction.

- (e) Two compounds combine to form a single product; this is a combination reaction.
- (f) The positive and negative ions change partners; this is a metathesis reaction. An acid and a base react to form a salt and water; this is an acid–base (neutralization) reaction.

You should now work Exercises 99 through 109.

Table 6-11 Summary and Examples of Reaction Types

Section Reaction Type, Examples		Characteristics
6-5	Oxidation–reduction (redox)	Oxidation states (see Section 5-7) of some elements change; at least one element must increase and at least one must decrease in oxidation states
6-6	Combination 1. element + element $\longrightarrow$ compound $2\text{Al(s)} + 3\text{Cl}_2\text{(g)} \longrightarrow 2\text{AlCl}_3\text{(s)}^*$ $\text{P}_4\text{(s)} + 10\text{Cl}_2\text{(g)} \longrightarrow 4\text{PCl}_5\text{(s)}^*$ 2. compound + element $\longrightarrow$ compound $\text{SF}_4\text{(g)} + \text{F}_2\text{(g)} \longrightarrow \text{SF}_6\text{(g)}^*$ $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \longrightarrow 2\text{SO}_3\text{(l)}^*$ 3. compound + compound $\longrightarrow$ compound $\text{CaO(s)} + \text{CO}_2\text{(g)} \longrightarrow \text{CaCO}_3\text{(s)}$ $\text{Na}_2\text{O(s)} + \text{H}_2\text{O(l)} \longrightarrow 2\text{NaOH(aq)}$	More than one reactant, single product
6-7	Decomposition 1. compound $\longrightarrow$ element + element $2\text{HgO(s)} \longrightarrow 2\text{Hg(l)} + \text{O}_2\text{(g)}^*$ $2\text{H}_2\text{O(l)} \longrightarrow 2\text{H}_2\text{(g)} + \text{O}_2\text{(g)}^*$ 2. compound $\longrightarrow$ compound + element $2\text{NaNO}_3\text{(s)} \longrightarrow 2\text{NaNO}_2\text{(s)} + \text{O}_2\text{(g)}^*$ $2\text{H}_2\text{O}_2\text{(l)} \longrightarrow 2\text{H}_2\text{O(l)} + \text{O}_2\text{(g)}^*$ 3. compound $\longrightarrow$ compound + compound $\text{CaCO}_3\text{(s)} \longrightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$ $\text{Mg(OH)}_2\text{(s)} \longrightarrow \text{MgO(s)} + \text{H}_2\text{O(l)}$	Single reactant, more than one product
6-8	Displacement $\text{Zn(s)} + \text{CuSO}_4\text{(aq)} \longrightarrow \text{Cu(s)} + \text{ZnSO}_4\text{(aq)}^*$ $\text{Zn(s)} + \text{H}_2\text{SO}_4\text{(aq)} \longrightarrow \text{H}_2\text{(g)} + \text{ZnSO}_4\text{(aq)}^*$ $\text{Cl}_2\text{(g)} + 2\text{NaI(aq)} \longrightarrow \text{I}_2\text{(s)} + 2\text{NaCl(aq)}^*$	One element displaces another from a compound: Element + compound $\longrightarrow$ element + compound Activity series (see Table 6-9) summarizes metals and hydrogen; halogen activities (Group 7A) decrease going down the group
6-9	Metathesis 1. acid–base neutralization $\text{HCl(aq)} + \text{NaOH(aq)} \longrightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$ $\text{CH}_3\text{COOH(aq)} + \text{KOH(aq)} \longrightarrow \text{KCH}_3\text{COO(aq)} + \text{H}_2\text{O(l)}$ $\text{HCl(aq)} + \text{NH}_3\text{(aq)} \longrightarrow \text{NH}_4\text{Cl(aq)}$ $2\text{H}_3\text{PO}_4\text{(aq)} + 3\text{Ca(OH)}_2\text{(aq)} \longrightarrow \text{Ca}_3\text{(PO}_4)_2\text{(s)} + 6\text{H}_2\text{O(l)}^\dagger$ 2. precipitation $\text{CaCl}_2\text{(aq)} + \text{Na}_2\text{CO}_3\text{(aq)} \longrightarrow \text{CaCO}_3\text{(s)} + 2\text{NaCl(aq)}$ $\text{Pb(NO}_3)_2\text{(aq)} + \text{K}_2\text{CrO}_4\text{(aq)} \longrightarrow \text{PbCrO}_4\text{(s)} + 2\text{KNO}_3\text{(aq)}$ $2\text{H}_3\text{PO}_4\text{(aq)} + 3\text{Ca(OH)}_2\text{(aq)} \longrightarrow \text{Ca}_3\text{(PO}_4)_2\text{(s)} + 6\text{H}_2\text{O(l)}^\dagger$	Positive and negative ions in two compounds appear to “change partners” to form two new compounds; no change in oxidation numbers Product is a salt; water is often formed Products include an insoluble substance, which precipitates from solution as a solid; solubility guidelines assist in predicting, recognizing
6-10	Gas-formation $2\text{HCl(aq)} + \text{CaCO}_3\text{(s)} \longrightarrow \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)} + \text{CaCl}_2\text{(aq)}$ $\text{MnS(s)} + 2\text{HCl(aq)} \longrightarrow \text{MnCl}_2\text{(aq)} + \text{H}_2\text{S(g)}$ $\text{Mg(s)} + 2\text{HNO}_3\text{(aq)} \longrightarrow \text{H}_2\text{(g)} + \text{Mg(NO}_3)_2\text{(aq)}$	Products include an insoluble or slightly soluble gas, which escapes from solution

*These examples are also oxidation–reduction (redox) reactions.

†This reaction is both an acid–base neutralization reaction and a precipitation reaction.

Unless otherwise noted, all content on this page is © Cengage Learning.

KEY TERMS

Acid A substance that produces $\text{H}^+(\text{aq})$ ions in aqueous solution. Strong acids ionize completely or almost completely in dilute aqueous solution. Weak acids ionize only slightly.

Acid–base reaction See *Neutralization reaction*.

Active metal A metal that readily loses electrons to form cations.

Activity series A listing of metals (and hydrogen) in order of decreasing activity.

Alkali metals Elements of Group 1A in the periodic table, except hydrogen.

Alkaline earth metals Group 2A elements in the periodic table.

Atomic number The number of protons in the nucleus of an atom of an element.

Base A substance that produces $\text{OH}^-(\text{aq})$ ions in aqueous solution. Strong bases are soluble in water and are completely dissociated. Weak bases ionize only slightly.

Binary acid A binary compound in which H is bonded to a nonmetal in Group 7A or a nonmetal other than oxygen in Group 6A.

Binary compound A compound consisting of two elements; may be ionic or molecular.

Combination reaction Reaction in which two substances (elements or compounds) combine to form one compound.

Decomposition reaction Reaction in which a compound decomposes to form two or more products (elements, compounds, or some combination of these).

Displacement reaction A reaction in which one element displaces another from a compound.

Disproportionation reaction A redox reaction in which the oxidizing agent and the reducing agent are the same element.

Dissociation In aqueous solution, the process in which a solid ionic compound separates into its ions.

Electrolyte A substance whose aqueous solutions conduct electricity due to ions in solution. Acids, bases, and soluble salts are electrolytes.

Formula unit equation An equation for a chemical reaction in which all formulas are written as complete formulas.

Gas-formation reaction A reaction in which an insoluble or slightly soluble gas is formed as a product.

Group (family) The elements in a vertical column of the periodic table.

Halogens Elements of Group 7A in the periodic table.

Ionization In aqueous solution, the process in which a molecular compound separates to form ions.

Metal An element below and to the left of the stepwise division (metalloids) of the periodic table; about 80% of the known elements are metals.

Metalloids Elements with properties intermediate between metals and nonmetals: B, Si, Ge, As, Sb, Te, Po, and At.

Metathesis reaction A reaction in which the positive and negative ions in two compounds “change partners,” with no change in oxidation numbers, to form two new compounds; also referred to as a *double displacement reaction*.

Net ionic equation An equation that results from canceling spectator ions from a total ionic equation.

Neutralization reaction The reaction of an acid with a base to form a salt. Often, the reaction of hydrogen ions with hydroxide ions to form water molecules.

Noble (rare) gases Elements of Group 8A in the periodic table.

Nonelectrolyte A substance whose aqueous solutions do not conduct electricity.

Nonmetals Elements above and to the right of the metalloids in the periodic table.

Oxidation An increase in oxidation number; corresponds to a loss of electrons.

Oxidation numbers See *Oxidation states*.

Oxidation–reduction reaction A reaction in which oxidation and reduction occur; also known as a redox reaction.

Oxidation states Arbitrary numbers that can be used as mechanical aids in writing formulas and balancing equations; for single-atom ions they correspond to the charge on the ion; less metallic atoms are assigned negative oxidation states in compounds and polyatomic ions.

Oxidizing agent The substance that oxidizes another substance and is reduced.

Oxoacid See *Ternary acid*.

Precipitate An insoluble solid that forms and separates from a solution.

Precipitation reaction A reaction in which a solid (precipitate) forms.

Redox reaction See *Oxidation–reduction reaction*.

Reducing agent The substance that reduces another substance and is oxidized.

Reduction A decrease in oxidation number; corresponds to a gain of electrons.

Reversible reaction A reaction that occurs in both directions; described with double arrows ($\rightleftharpoons$). The equal-length arrows do not indicate equal amounts of reactants and products, just that some of each are present. Chemists sometimes indicate the favored direction of a reversible reaction by using a longer arrow on top or bottom ($\rightleftharpoons$, $\rightleftharpoons$).

Salt An ionic compound that contains a cation other than H^+ and an anion other than OH^- or O^{2-} .

Semiconductor A substance that does not conduct electricity at low temperatures but does so at higher temperatures.

Spectator ions Ions that appear in solution on both sides of the total ionic equation; they undergo no change in the chemical reaction.

Strong acid An acid that ionizes (separates into ions) completely, or very nearly completely, in dilute aqueous solution.

Strong base Metal hydroxide that is soluble in water and dissociates completely in dilute aqueous solution.

Strong electrolyte A substance that conducts electricity well in dilute aqueous solution due to nearly complete ionization or dissociation.

Ternary acid A ternary compound containing H, O, and another element, usually a nonmetal; also known as an *oxoacid*.

Ternary compound A compound consisting of three elements; may be ionic or molecular.

Ternary salt A salt resulting from replacing the hydrogen in a ternary acid with another ion.

Total ionic equation An equation for a chemical reaction written to show the predominant form of all species in aqueous solution or in contact with water.

Weak acid An acid that ionizes only slightly in dilute aqueous solution.

Weak base A molecular substance that ionizes only slightly in water to produce an alkaline (base) solution.

Weak electrolyte A substance that conducts electricity poorly in dilute aqueous solution due to very limited ionization or dissociation.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Aqueous Solutions

- Similar to the inserts in Figure 6-1, draw molecular representations of a solution of a strong electrolyte, of a weak electrolyte, and of a nonelectrolyte.
- Three common classes of compounds are electrolytes. Name them and give an example of each.
- Define (a) acids, (b) bases, (c) salts, and (d) molecular compounds.
- How can a salt be related to a particular acid and a particular base?
- List the names and formulas of three common strong acids.
- Write equations for the ionization of the following acids: (a) hydrochloric acid; (b) nitric acid; (c) chlorous acid; (d) carbonic acid.
- List the names and formulas of five weak acids.
- List the names and formulas of the common strong bases.
- Write equations for the ionization of the following acids. Which ones ionize only slightly? (a) HF; (b) HCN; (c) CH_3COOH ; (d) HClO_3 ; (e) HBr.
- The most common weak base is present in a common household chemical. Write the equation for the ionization of this weak base.
- Summarize the electrical properties of strong electrolytes, weak electrolytes, and nonelectrolytes.
- What is the difference between ionization and dissociation in aqueous solution?
- Predict whether each of these compounds is likely to be water-soluble. Indicate which ions are present in solution for the water-soluble compounds. (a) $\text{Fe}(\text{ClO}_4)_2$; (b) Na_2SO_4 ; (c) KBr; (d) Na_2CO_3 .
- Which of the following are strong electrolytes? weak electrolytes? nonelectrolytes? (a) Na_2S ; (b) $\text{Ba}(\text{OH})_2$; (c) CH_3OH ; (d) HCN; (e) $\text{Al}(\text{NO}_3)_3$. Write equations that show the dissociation of the strong electrolytes.
- Classify the following as strong electrolytes, weak electrolytes, or nonelectrolytes: (a) NaClO_4 ; (b) HClO_2 ; (c) $\text{CH}_3\text{CH}_2\text{OH}$; (d) CH_3COOH ; (e) HNO_3 . Write equations that show the dissociation of the strong electrolytes.
- Write the formulas of two soluble and two insoluble chlorides, sulfates, and hydroxides.
- Describe an experiment for classifying each of these compounds as a strong electrolyte, a weak electrolyte, or a nonelectrolyte: Na_2CO_3 , HCN, CH_3OH , H_2S , H_2SO_4 , NH_3 . Predict and explain the expected results.
- Classify the following compounds as acids or bases, weak or strong: (a) perchloric acid; (b) cesium hydroxide; (c) carbonic acid; H_2CO_3 ; (d) ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$.
- ▲ Classify each substance as either an electrolyte or a nonelectrolyte: NH_4Cl , HCl, C_6H_6 , $\text{Zn}(\text{CH}_3\text{COO})_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{CH}_3\text{CH}_2\text{OH}$, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (sugar), LiOH, KHCO_3 , CCl_4 , K_2SO_4 , I_2 .
- What is an electrolyte? How can you differentiate experimentally between a weak electrolyte and a strong electrolyte? Give an example of each.
- Classify each substance as soluble, moderately soluble, or insoluble: Ag_2SO_4 , $(\text{NH}_4)_2\text{CO}_3$, AgCl, HgBr_2 , AgNO_3 .
- Classify each substance as soluble, moderately soluble, or insoluble: $\text{Ca}(\text{CH}_3\text{COO})_2$, NH_4Cl , AgNO_3 , PbCl_2 , $(\text{NH}_4)_3\text{PO}_4$.
- What are reversible reactions? Give some examples that illustrate reversible reactions at the molecular level.
- Many household “chemicals” are acidic or basic. List a few of each kind.
- Some chemical reactions reach an equilibrium rather than going to completion. What is “equal” in such an equilibrium? Use equations to illustrate “equal” at the molecular level in an equilibrium reaction.
- Vinegar is 5% acetic acid, an organic acid, by mass. Many organic acids occur in living systems. What conclusion can be drawn from this information as to the strengths of organic acids?

Naming Compounds

- Name the following common anions using the IUPAC system of nomenclature: (a) NO_3^- ; (b) SO_4^{2-} ; (c) ClO_3^- ; (d) CH_3COO^- ; (e) PO_4^{3-} .
- Name the following monatomic cations using the IUPAC system of nomenclature: (a) Li^+ ; (b) Au^{3+} ; (c) Ca^{2+} ; (d) Zn^{2+} ; (e) Ag^+ .
- Write the chemical symbol for each of the following: (a) sodium ion; (b) iron(II) ion; (c) silver ion; (d) mercury(II) ion; (e) bismuth(III) ion.
- Write the chemical formula for each of the following: (a) chloride ion; (b) hydrogen sulfide ion; (c) telluride ion; (d) hydroxide ion; (e) nitrite ion.

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

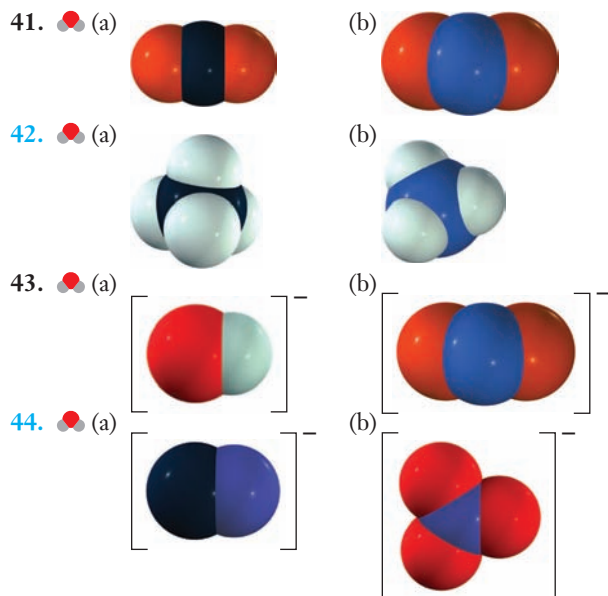
Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

31. Name the following compounds: (a) Li_2S ; (b) SnO_2 ; (c) RbBr ; (d) K_2O ; (e) Ba_3N_2 .
32. Name the following compounds: (a) CuI_2 ; (b) Hg_2Cl_2 ; (c) Li_3N ; (d) MnCl_2 ; (e) CuCO_3 ; (f) FeO .
33. Write the chemical formula for each of the following compounds: (a) lithium fluoride; (b) zinc oxide; (c) barium hydroxide; (d) magnesium bromide; (e) hydrogen cyanide; (f) copper(I) chloride.
34. Write the chemical formula for each of the following compounds: (a) copper(II) chlorite; (b) potassium nitrate; (c) barium phosphate; (d) copper(I) sulfate; (e) sodium sulfite.
35. What is the name of the acid with the formula H_2CO_3 ? Write the formulas of the two anions derived from it and name these ions.
36. What is the name of the acid with the formula H_3PO_4 ? What are the names of the ions: H_2PO_4^- ; HPO_4^{2-} ; PO_4^{3-} ?
37. Name the following binary molecular compounds: (a) NO_2 ; (b) CO_2 ; (c) SF_6 ; (d) SiCl_4 ; (e) IF .
38. Name the following binary molecular compounds: (a) AF_3 ; (b) Br_2O ; (c) BrF_5 ; (d) CSe_2 ; (e) N_2O_4 .
39. Write the chemical formula for each of the following compounds: (a) iodine bromide; (b) silicon dioxide; (c) phosphorus trichloride; (d) tetrasulfur dinitride; (e) bromine trifluoride; (f) hydrogen telluride; (g) xenon tetrafluoride.
40. Write the chemical formula for each of the following compounds: (a) diboron trioxide; (b) dinitrogen pentasulfide; (c) phosphorus triiodide; (d) sulfur tetrafluoride; (e) silicon sulfide; (f) hydrogen sulfide; (g) tetraphosphorus hexoxide.

In Exercises 41 through 44, write the name and the formula of the compound or ion represented by each model.

Black = C, white = H, red = O, and blue = nitrogen.



45. Write formulas for the compounds that are expected to be formed by the following pairs of ions:

	A. Br^-	B. OH^-	C. SO_4^{2-}	D. PO_4^{3-}	E. NO_3^-
1. NH_4^+		Omit – see note			
2. Na^+					
3. Mg^{2+}					
4. Cu^{2+}					
5. Fe^{3+}					
6. Ag^+					

Note: The compound NH_4OH does not exist. The solution commonly labeled “ NH_4OH ” is aqueous ammonia, $\text{NH}_3(\text{aq})$.

46. Write the names for the compounds of Exercise 45.
47. Write balanced chemical equations for each of the following processes: (a) Calcium phosphate reacts with sulfuric acid to produce calcium sulfate and phosphoric acid. (b) Calcium phosphate reacts with water containing dissolved carbon dioxide to produce calcium hydrogen carbonate and calcium hydrogen phosphate.
48. Write balanced chemical equations for each of the following processes: (a) When heated, nitrogen and oxygen combine to form nitrogen oxide. (b) Heating a mixture of lead(II) sulfide and lead(II) sulfate produces metallic lead and sulfur dioxide.

Oxidation–Reduction Reactions

49. Define and provide examples of the following terms: (a) oxidation; (b) reduction; (c) oxidizing agent; (d) reducing agent.
50. Why must oxidation and reduction always occur simultaneously in chemical reactions?
51. Determine which of the following are oxidation–reduction reactions. For those that are, identify the oxidizing and reducing agents.
- (a) $3\text{Zn}(\text{s}) + 2\text{CoCl}_2(\text{aq}) \longrightarrow 3\text{ZnCl}_2(\text{aq}) + 2\text{Co}(\text{s})$
- (b) $\text{ICl}(\text{s}) + \text{H}_2\text{O}(\ell) \longrightarrow \text{HCl}(\text{aq}) + \text{HIO}(\text{aq})$
- (c) $3\text{HCl}(\text{aq}) + \text{HNO}_3(\text{aq}) \longrightarrow \text{Cl}_2(\text{g}) + \text{NOCl}(\text{g}) + 2\text{H}_2\text{O}(\ell)$
- (d) $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \xrightarrow{\text{heat}} 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$
52. Determine which of the following are oxidation–reduction reactions. For those that are, identify the oxidizing and reducing agents.
- (a) $\text{HgCl}_2(\text{aq}) + 2\text{KI}(\text{aq}) \longrightarrow \text{HgI}_2(\text{s}) + 2\text{KCl}(\text{aq})$
- (b) $4\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- (c) $\text{CaCO}_3(\text{s}) + 2\text{HNO}_3(\text{aq}) \longrightarrow \text{Ca}(\text{NO}_3)_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell)$
- (d) $\text{PCl}_3(\ell) + 3\text{H}_2\text{O}(\ell) \longrightarrow 3\text{HCl}(\text{aq}) + \text{H}_3\text{PO}_3(\text{aq})$

53. Write balanced formula unit equations for the following redox reactions:
- aluminum reacts with sulfuric acid, H_2SO_4 , to produce aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, and hydrogen;
 - nitrogen, N_2 , reacts with hydrogen, H_2 , to form ammonia, NH_3 ;
 - zinc sulfide, ZnS , reacts with oxygen, O_2 , to form zinc oxide, ZnO , and sulfur dioxide, SO_2 ;
 - carbon reacts with nitric acid, HNO_3 , to produce nitrogen dioxide, NO_2 , carbon dioxide, CO_2 , and water;
 - sulfuric acid reacts with hydrogen iodide, HI , to produce sulfur dioxide, SO_2 , iodine, I_2 , and water.
54. Identify the oxidizing agents and reducing agents in the oxidation–reduction reactions given in Exercise 53.
55. Write total ionic and net ionic equations for the following redox reactions occurring in aqueous solution or in contact with water:
- $\text{Fe} + 2\text{HCl} \longrightarrow \text{FeCl}_2 + \text{H}_2$
 - $2\text{KMnO}_4 + 16\text{HCl} \longrightarrow 2\text{MnCl}_2 + 2\text{KCl} + 5\text{Cl}_2 + 8\text{H}_2\text{O}$
- (Note: MnCl_2 is water-soluble.)
- $4\text{Zn} + 10\text{HNO}_3 \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}$

56. Balance each of these equations, and then write the complete ionic and net ionic equations.
- $\text{Zn}(\text{s}) + \text{HCl}(\text{aq}) \longrightarrow \text{H}_2(\text{g}) + \text{ZnCl}_2(\text{aq})$
 - $\text{Mg}(\text{OH})_2(\text{s}) + \text{HCl}(\text{aq}) \longrightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\ell)$
 - $\text{HNO}_3(\text{aq}) + \text{CaCO}_3(\text{s}) \longrightarrow \text{Ca}(\text{NO}_3)_2(\text{aq}) + \text{H}_2\text{O}(\ell) + \text{CO}_2(\text{g})$
 - $\text{HCl}(\text{aq}) + \text{MnO}_2(\text{s}) \longrightarrow \text{MnCl}_2(\text{aq}) + \text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\ell)$

Combination Reactions

57. Write balanced equations that show the combination reactions of the following Group 1A metals combining with the Group 7A nonmetals. (a) Li and Cl_2 ; (b) K and F_2 ; (c) Na and I_2 .
58. Write balanced equations that show the combination reactions of the following Group 2A metals and Group 7A nonmetals. (a) Be and F_2 ; (b) Ca and Br_2 ; (c) Ba and Cl_2 .

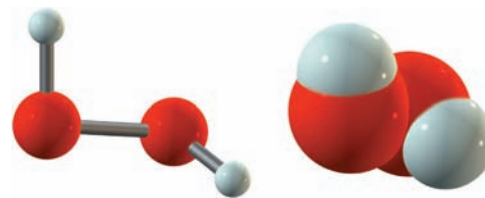
In Exercises 59 and 60, some combination reactions are described by words. Write the balanced chemical equation for each, and assign oxidation states to elements other than H and O.

59. (a) Antimony reacts with a limited amount of chlorine to form antimony(III) chloride. (b) Antimony(III) chloride reacts with excess chlorine to form antimony(V) chloride. (c) Carbon burns in a limited amount of oxygen to form carbon monoxide.
60. (a) Sulfur trioxide reacts with aluminum oxide to form aluminum sulfate. (b) Dichlorine heptoxide reacts with water to form perchloric acid. (c) When cement “sets,” the main reaction is the combination of calcium oxide with silicon dioxide to form calcium silicate, CaSiO_3 .

Decomposition Reactions

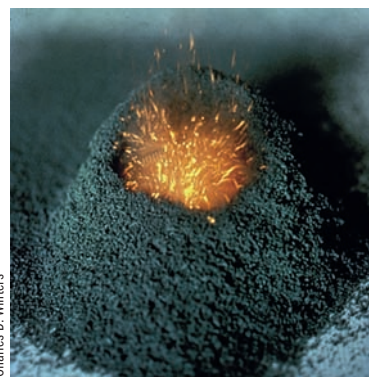
In Exercises 61 and 62, write balanced formula unit equations for the reactions described by words. Assign oxidation states to all elements.

61. (a) Hydrogen peroxide, H_2O_2 , is used as an antiseptic. Blood causes it to decompose into water and oxygen. (b) When heated, ammonium nitrate can decompose explosively to form dinitrogen oxide and steam.



Models of hydrogen peroxide

62. (a) A “classroom volcano” is made by heating solid ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, which decomposes into nitrogen, chromium(III) oxide, and steam. (b) At high temperatures, sodium nitrate (a fertilizer) forms sodium nitrite and oxygen.



Charles D. Winters

Ammonium dichromate volcano

Displacement Reactions

63. Which of the following would displace hydrogen when a piece of the metal is dropped into dilute HCl solution? Write balanced total ionic and net ionic equations for the reactions: Zn, Cu, Sn, Al.
64. Which of the following metals would displace copper from an aqueous solution of copper(II) sulfate? Write balanced total ionic and net ionic equations for the reactions: Hg, Zn, Fe, Ni.
65. Arrange the metals listed in Exercise 63 in order of increasing activity.
66. Arrange the metals listed in Exercise 64 in order of increasing activity.
67. Which of the following metals would displace hydrogen from cold water? Write balanced net ionic equations for the reactions: Ag, Na, Ca, Cr.
68. Arrange the metals listed in Exercise 67 in order of increasing activity.



69. What is the order of decreasing activity of the halogens?
70. Name five elements that will react with steam but not with cold water.
71. (a) Name two common metals: one that *does not* displace hydrogen from water, and one that *does not* displace hydrogen from water or acid solutions. (b) Name two common metals: one that *does* displace hydrogen from water, and one that displaces hydrogen from acid solutions but not from water. Write net ionic equations for the reactions that occur.
72. Of the possible displacement reactions shown, which one(s) could occur?
- (a) $2\text{Cl}^-(\text{aq}) + \text{Br}_2(\ell) \longrightarrow 2\text{Br}^-(\text{aq}) + \text{Cl}_2(\text{g})$
 (b) $2\text{Br}^-(\text{aq}) + \text{F}_2(\text{g}) \longrightarrow 2\text{F}^-(\text{aq}) + \text{Br}_2(\ell)$
 (c) $2\text{I}^-(\text{aq}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl}^-(\text{aq}) + \text{I}_2(\text{s})$
 (d) $2\text{Br}^-(\text{aq}) + \text{I}_2(\text{s}) \longrightarrow 2\text{I}^-(\text{aq}) + \text{Br}_2(\ell)$
73. Use the activity series to predict whether or not the following reactions will occur:
- (a) $\text{Cu}(\text{s}) + \text{Pt}^{2+} \longrightarrow \text{Pt}(\text{s}) + \text{Cu}^{2+}$
 (b) $\text{Ni}(\text{s}) + \text{Cu}^{2+} \longrightarrow \text{Ni}^{2+} + \text{Cu}(\text{s})$
 (c) $\text{Cu}(\text{s}) + 2\text{H}^+ \longrightarrow \text{Cu}^{2+} + \text{H}_2(\text{g})$
 (d) $\text{Ni}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{NiO}(\text{s}) + \text{H}_2(\text{g})$
74. Repeat Exercise 73 for
- (a) $\text{Cd}(\text{s}) + \text{Ca}^{2+} \longrightarrow \text{Cd}^{2+} + \text{Ca}(\text{s})$
 (b) $\text{Al}_2\text{O}_3(\text{s}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{Al}(\text{s}) + 3\text{H}_2\text{O}(\text{g})$
 (c) $\text{Zn}(\text{s}) + 2\text{H}^+ \longrightarrow \text{Zn}^{2+} + \text{H}_2(\text{g})$
 (d) $\text{Zn}(\text{s}) + \text{Pb}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Pb}(\text{s})$

Metathesis Reactions

Exercises 75 and 76 describe precipitation reactions *in aqueous solutions*. For each, write balanced (i) formula unit, (ii) total ionic, and (iii) net ionic equations. Refer to the solubility guidelines as necessary.

75. (a) Black-and-white photographic film contains some silver bromide, which can be formed by the reaction of sodium bromide with silver nitrate. (b) Barium sulfate is used when X-rays of the gastrointestinal tract are made. Barium sulfate can be prepared by reacting barium chloride with dilute sulfuric acid. (c) In water purification systems small solid particles are often “trapped” as aluminum hydroxide precipitates and fall to the bottom of the sedimentation pool. Aluminum sulfate reacts with calcium hydroxide (from lime) to form aluminum hydroxide and calcium sulfate.
76. (a) Our bones are mostly calcium phosphate. Calcium chloride reacts with potassium phosphate to form calcium phosphate and potassium chloride. (b) Mercury compounds are very poisonous. Mercury(II) nitrate reacts with sodium sulfide to form mercury(II) sulfide, which is very insoluble, and sodium nitrate. (c) Chromium(III) ions are very poisonous. They can be removed from solution by precipitating very insoluble chromium(III) hydroxide. Chromium(III) chloride reacts with calcium hydroxide to form chromium(III) hydroxide and calcium chloride.

In Exercises 77 through 80, write balanced (i) formula unit, (ii) total ionic, and (iii) net ionic equations for the reactions that occur between the acid and the base. Assume that all reactions occur in water or in contact with water.

77. (a) hydrochloric acid + calcium hydroxide
 (b) dilute sulfuric acid + strontium hydroxide
 (c) perchloric acid + aqueous ammonia
78. (a) acetic acid + potassium hydroxide
 (b) sulfurous acid + sodium hydroxide
 (c) hydrofluoric acid + sodium hydroxide
79. (a) potassium hydroxide + hydrosulfuric acid
 (b) potassium hydroxide + hydrochloric acid
 (c) lead(II) hydroxide + hydrosulfuric acid
80. (a) lithium hydroxide + sulfuric acid
 (b) calcium hydroxide + phosphoric acid
 (c) copper(II) hydroxide + nitric acid

In Exercises 81 through 84, write balanced (i) formula unit, (ii) total ionic, and (iii) net ionic equations for the reaction of an acid and a base that will produce the indicated salts.

81. (a) potassium chloride; (b) sodium nitrate; (c) barium sulfate
82. (a) calcium perchlorate; (b) ammonium sulfate; (c) copper(II) acetate
83. (a) sodium carbonate; (b) barium carbonate; (c) nickel(II) acetate
84. (a) sodium sulfide; (b) aluminum phosphate; (c) lead(II) carbonate
85. (a) Propose a definition for salts, as a class of compounds, on the basis of how they are formed. (b) Provide an example, in the form of a chemical reaction, to illustrate your definition of salts.
86. We can tell from the formula of a salt how it can be produced. Write a balanced chemical equation for the production of each of the following salts: (a) magnesium nitrate; (b) aluminum sulfite; (c) potassium carbonate; (d) zinc chlorate; (e) lithium acetate.
87. Magnesium hydroxide is a gelatinous material that forms during the water purification process in some water treatment plants because of magnesium ions in the water. (a) Write the chemical equation for the reaction of hydrochloric acid with magnesium hydroxide. (b) Explain what drives this reaction to completion.

Precipitation Reactions

88. A common test for the presence of chloride ions is the formation of a heavy, white precipitate when a solution of silver nitrate is added. (a) Write the balanced chemical equation for the production of silver chloride from silver nitrate solution and calcium chloride solution. (b) Explain why this reaction goes to completion.
89. Based on the solubility guidelines given in Table 6-4, how would you write the formulas for the following substances in a total ionic equation? (a) PbSO_4 ; (b) $\text{Na}(\text{CH}_3\text{COO})$; (c) Na_2CO_3 ; (d) MnS ; (e) BaCl_2 .

90. Repeat Exercise 89 for the following: (a) $(\text{NH}_4)_2\text{SO}_4$; (b) NaBr ; (c) SrCl_2 ; (d) MgF_2 ; (e) Na_2CO_3 .

Refer to the solubility guidelines given in Table 6-4. Classify the compounds in Exercises 91 through 94 as soluble, moderately soluble, or insoluble in water.

91. (a) NaClO_4 , (b) AgCl , (c) $\text{Pb}(\text{NO}_3)_2$, (d) KOH , (e) CaSO_4
 92. (a) BaSO_4 , (b) $\text{Al}(\text{NO}_3)_3$, (c) CuS , (d) Na_3AsO_4 , (e) $\text{Ca}(\text{CH}_3\text{COO})_2$
 93. (a) $\text{Fe}(\text{NO}_3)_3$, (b) $\text{Hg}(\text{CH}_3\text{COO})_2$, (c) BeCl_2 , (d) CuSO_4 , (e) CaCO_3
 94. (a) KClO_3 , (b) NH_4Cl , (c) NH_3 , (d) HNO_2 , (e) PbS

In Exercises 95 and 96, write balanced (i) formula unit, (ii) total ionic, and (iii) net ionic equations for the reactions that occur when *aqueous solutions* of the compounds are mixed.

95. (a) $\text{Ba}(\text{NO}_3)_2 + \text{K}_2\text{CO}_3 \longrightarrow$
 (b) $\text{NaOH} + \text{NiCl}_2 \longrightarrow$
 (c) $\text{Al}_2(\text{SO}_4)_3 + \text{NaOH} \longrightarrow$
 96. (a) $\text{Cu}(\text{NO}_3)_2 + \text{Na}_2\text{S} \longrightarrow$
 (b) $\text{CdSO}_4 + \text{H}_2\text{S} \longrightarrow$
 (c) $\text{Bi}_2(\text{SO}_4)_3 + (\text{NH}_4)_2\text{S} \longrightarrow$
 97. In each of the following, both compounds are water-soluble. Predict whether a precipitate will form when solutions of the two are mixed, and, if so, identify the compound that precipitates. (a) $\text{Pb}(\text{NO}_3)_2$, NaI ; (b) $\text{Ba}(\text{NO}_3)_2$, KCl ; (c) $(\text{NH}_4)_2\text{S}$, AgNO_3 .
 98. Classify each of these exchange reactions as an acid-base reaction, a precipitation reaction, or a gas-forming reaction. Predict the products of the reaction, and then balance the completed equation.
 (a) $\text{MnCl}_2(\text{aq}) + \text{Na}_2\text{S}(\text{aq}) \longrightarrow$
 (b) $\text{Na}_2\text{CO}_3(\text{aq}) + \text{ZnCl}_2(\text{aq}) \longrightarrow$
 (c) $\text{K}_2\text{CO}_3(\text{aq}) + \text{HClO}_4(\text{aq}) \longrightarrow$

Identifying Reaction Types

The following reactions apply to Exercises 99 through 109.

- (a) $\text{H}_2\text{SO}_4(\text{aq}) + 2\text{KOH}(\text{aq}) \longrightarrow \text{K}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\ell)$
 (b) $2\text{Rb}(\text{s}) + \text{Br}_2(\ell) \xrightarrow{\text{heat}} 2\text{RbBr}(\text{s})$
 (c) $2\text{KI}(\text{aq}) + \text{F}_2(\text{g}) \longrightarrow 2\text{KF}(\text{aq}) + \text{I}_2(\text{s})$
 (d) $\text{CaO}(\text{s}) + \text{SiO}_2(\text{s}) \xrightarrow{\text{heat}} \text{CaSiO}_3(\text{s})$
 (e) $\text{S}(\text{s}) + \text{O}_2(\text{g}) \xrightarrow{\text{heat}} \text{SO}_2(\text{g})$
 (f) $\text{BaCO}_3(\text{s}) \xrightarrow{\text{heat}} \text{BaO}(\text{s}) + \text{CO}_2(\text{g})$
 (g) $\text{HgS}(\text{s}) + \text{O}_2(\text{g}) \xrightarrow{\text{heat}} \text{Hg}(\ell) + \text{SO}_2(\text{g})$
 (h) $\text{AgNO}_3(\text{aq}) + \text{HCl}(\text{aq}) \longrightarrow \text{AgCl}(\text{s}) + \text{HNO}_3(\text{aq})$
 (i) $\text{Pb}(\text{s}) + 2\text{HBr}(\text{aq}) \longrightarrow \text{PbBr}_2(\text{s}) + \text{H}_2(\text{g})$
 (j) $2\text{HI}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \longrightarrow \text{I}_2(\text{s}) + 2\text{H}_2\text{O}(\ell)$
 (k) $\text{RbOH}(\text{aq}) + \text{HNO}_3(\text{aq}) \longrightarrow \text{RbNO}_3(\text{aq}) + \text{H}_2\text{O}(\ell)$
 (l) $\text{N}_2\text{O}_5(\text{s}) + \text{H}_2\text{O}(\ell) \longrightarrow 2\text{HNO}_3(\text{aq})$
 (m) $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \xrightarrow{\text{heat}} \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$
 (n) $\text{MgO}(\text{s}) + \text{H}_2\text{O}(\ell) \longrightarrow \text{Mg}(\text{OH})_2(\text{s})$
 (o) $\text{PbSO}_4(\text{s}) + \text{PbS}(\text{s}) \xrightarrow{\text{heat}} 2\text{Pb}(\text{s}) + 2\text{SO}_2(\text{g})$

99. Identify the precipitation reactions.
 100. Identify the acid–base reactions.
 101. Identify the oxidation–reduction reactions.
 102. Identify the oxidizing agent and reducing agent for each oxidation–reduction reaction.
 103. Identify the displacement reactions.
 104. Identify the metathesis reactions.
 105. Identify the combination reactions.
 106. Identify the decomposition reactions.
 107. Identify the gas-formation reactions.
 108. (a) Identify the oxidation–reduction reactions that form gaseous products, whether or not they can be classified as gas-formation reactions. (b) Which of these also fit the definition of gas-formation reactions? Why?
 109. (a) Do any of these reactions fit into more than one class? Which ones? (b) Do any of these reactions not fit into any of our classes of reactions? Which ones?
 110. Predict whether or not a solid is formed when we mix the following; identify any solid product by name and identify the reaction type: (a) copper(II) nitrate solution and magnesium metal; (b) barium nitrate and sodium phosphate solutions; (c) calcium acetate solution and aluminum metal; (d) silver nitrate and sodium iodide solutions.
 111. Predict whether or not a solid is formed when we mix the following; identify any solid product by formula and by name: (a) potassium permanganate and sodium phosphate solutions; (b) lithium carbonate and cadmium nitrate solutions; (c) stannous fluoride and bismuth chloride solutions; (d) strontium sulfate and barium chloride solutions.

Conceptual Exercises

112. Each of the following statements is incorrect. Explain why.
 (a) A 1.2 M CH_3COOH solution is a stronger acid than a 0.12 M CH_3COOH solution. (b) The salt produced during the neutralization of nitric acid with potassium hydroxide is KNO_4 . (c) Nickel will react with a HCl solution but not with steam to produce hydrogen and nickel ion solution. Magnesium will react with steam to produce hydrogen and magnesium ions. Therefore, nickel is more reactive than magnesium.
 113. Determine the oxidation state of bromine in each of the following: (a) Br_2 ; (b) Br^- ; (c) KBr ; (d) BrCl ; (e) PBr_5 ; (f) BrO_3^- . In which of these species is the charge on the bromine actually the same as its oxidation state?
 114. Which of the following types of reactions is *always* an oxidation–reduction reaction: combination, decomposition, displacement, and metathesis? Which of these types of reactions is *never* an oxidation–reduction reaction?

As we have seen, two substances may react to form different products when they are mixed in different proportions under different conditions. In Exercises 115 and 116, write balanced equations for the reactions described by words. Assign oxidation states.

115. (a) Ethane burns in excess air to form carbon dioxide and water. (b) Ethane burns in a limited amount of air to form carbon monoxide and water. (c) Ethane burns (poorly) in a very limited amount of air to form elemental carbon and water.



116. (a) Butane (C_4H_{10}) burns in excess air to form carbon dioxide and water. (b) Butane burns in a limited amount of air to form carbon monoxide and water. (c) When heated in the presence of *very little* air, butane “cracks” to form acetylene, C_2H_2 , carbon monoxide, and hydrogen.
117. Calcium phosphate is the component of human bone that provides rigidity. Fallout from a nuclear bomb can contain radioactive strontium-90. These two facts are closely tied together when one considers human health. Explain.
118. Limestone consists mainly of the mineral calcite, which is calcium carbonate. A very similar deposit called dolostone is composed primarily of the mineral dolomite, an ionic substance that contains carbonate ions and a mixture of magnesium and calcium ions. (a) Is this a surprising mixture of ions? Explain, based on the periodic table. (b) A test for limestone is to apply cold dilute hydrochloric acid, which causes the rapid formation of bubbles. What causes these bubbles?

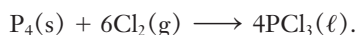


The Dolomite Alps of Italy

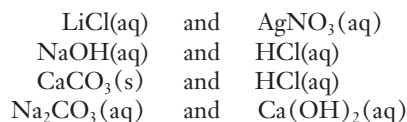
119. Chemical equations can be interpreted on either a particulate level (atoms, molecules, ions) or a mole level (moles of reactants and products). Write word statements to describe the combustion of propane on a particulate level and a mole level.



120. Write word statements to describe the following reaction on a particulate level and a mole level:



121. When the following pairs of reactants are combined in a beaker: (a) describe in words what the contents of the beaker would look like before and after any reaction that might occur; (b) use different circles for different types of atoms, molecules, and ions to draw a nanoscale (particulate-level) diagram of what the contents would look like; and (c) write a chemical equation for any reactions that might occur.



122. Nitric acid reacts with strontium hydroxide producing soluble strontium nitrate and water. Write the balanced formula unit equation, the total ionic equation, and the net ionic equation for this reaction. Sulfuric acid reacts with rubidium hydroxide producing soluble rubidium sulfate and water. Write the balanced formula unit equation, the total ionic equation, and the net ionic equation for this reaction. What do the net ionic equations for these two reactions have in common?

123. Suppose solutions of magnesium acetate and potassium sulfide were mixed. If a reaction occurred, the products would be magnesium sulfide and potassium acetate, both of which are soluble. Write the balanced formula unit equation, the total ionic equation, and the net ionic equation for this reaction. Did you get the same net ionic equation as you obtained in Exercise 122? Explain your finding.
124. Explain how you could prepare barium sulfate by (a) an acid-base reaction, (b) a precipitation reaction, and (c) a gas-forming reaction. The materials you have to start with are BaCO_3 , $\text{Ba}(\text{OH})_2$, Na_2SO_4 , and H_2SO_4 .
125. When acetic acid, CH_3COOH , is dissolved in water, 0.5% of the acetic acid molecules ionize:



Standard vinegar is 5.0% acetic acid by mass. Draw models illustrating the components in vinegar (include a model for water). Given that the density of the vinegar is about 1.01 g/mL, calculate the mass of 1.0 L of vinegar. What masses of the acetic acid and water are present? Convert the mass of the acetic acid to moles. Given that 0.50% of the acetic acid ionizes, how many moles each of hydrogen ion and acetate ion are produced? Calculate the molarity of the acid and of each of the ions. Convert the mass of the water to moles. What is the molar concentration of the water? Which component of the solution has the largest concentration?

126. Some types of chemical reactions are sometimes represented by general equations that don't represent any specific substances or reactions but illustrate key characteristics that are common to that type of reaction. What type of reaction might be represented by each of the following general equations:
(a) $\text{AB} + \text{CD} \longrightarrow \text{AD} + \text{CB}$, (b) $\text{AB} \longrightarrow \text{A} + \text{B}$,
(c) $\text{A} + \text{BC} \longrightarrow \text{AC} + \text{B}$, and (d) $\text{A} + \text{B} \longrightarrow \text{AB}$?

Building Your Knowledge

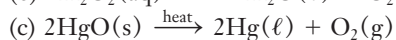
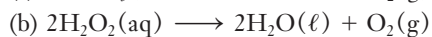
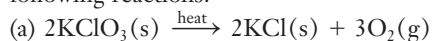
127. Magnesium oxide, marketed as tablets or as an aqueous slurry called “milk of magnesia,” is a common commercial antacid. What volume, in milliliters, of fresh gastric juice, corresponding in acidity to 0.17 M HCl, could be neutralized by 104 mg of magnesium oxide?



Charles D. Winters

Milk of magnesia

128. How many moles of oxygen can be obtained by the decomposition of 24.0 grams of reactant in each of the following reactions?



Beyond the Textbook

NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.*

129. Go to www.nist.gov, then click on “General Information.”

- (a) What does NIST stand for?
(b) What is the mission of NIST?

130. Go to www.nrc.gov, then click on “who we are.”

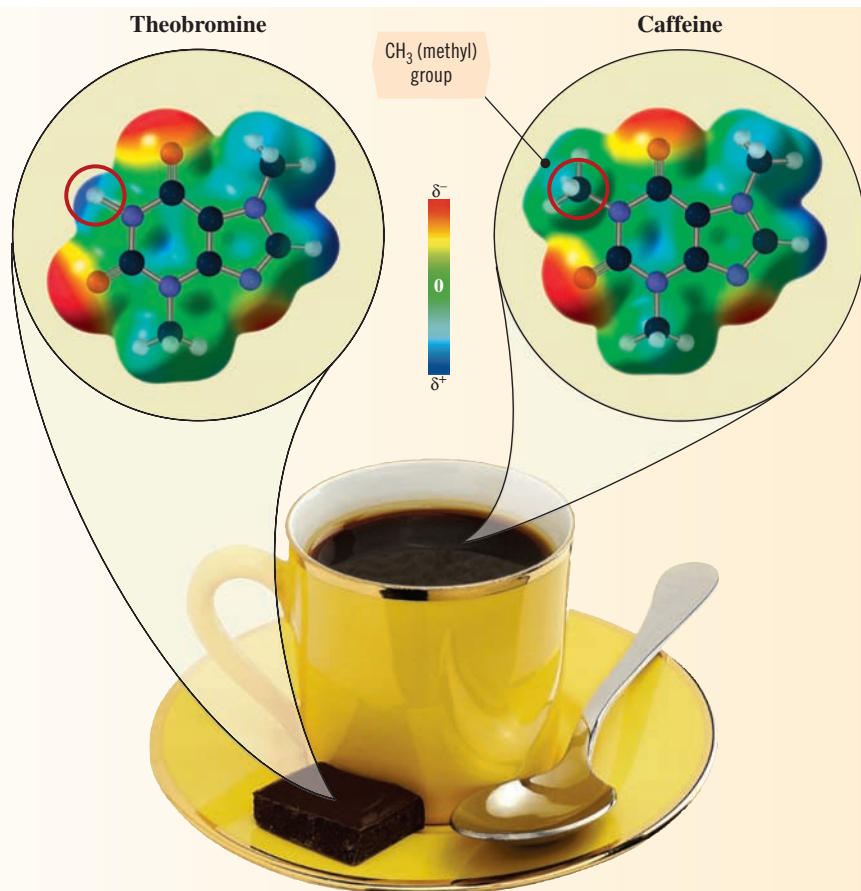
- (a) What does NRC stand for?
(b) What is the mission of NRC?

131. In *The Merck Index* and at various sites on the web one can find descriptions of small and large compounds that utilize terms not normally found in general chemistry textbooks. These terms include acidulant, astringent, diuretic, and expectorant. Describe each of these four properties.



Chemical Bonding

7



The main stimulants in chocolate and coffee are closely related chemicals—theobromine and caffeine, respectively. The structural difference is circled in the two molecular drawings. Theobromine is a milder stimulant that lasts longer than caffeine and has a mood improving effect.

© Iconotec/Alamy

OUTLINE

7-1 Lewis Dot Formulas of Atoms

Ionic Bonding

7-2 Formation of Ionic Compounds

Covalent Bonding

7-3 Formation of Covalent Bonds

7-4 Bond Lengths and Bond Energies

7-5 Lewis Formulas for Molecules and Polyatomic Ions

7-6 Writing Lewis Formulas: The Octet Rule

7-7 Formal Charges

7-8 Writing Lewis Formulas: Limitations of the Octet Rule

7-9 Resonance

7-10 Polar and Nonpolar Covalent Bonds

7-11 Dipole Moments

7-12 The Continuous Range of Bonding Types

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Write Lewis dot representations of atoms
- ▶ Predict whether bonding between specified elements will be primarily ionic, nonpolar covalent, or polar covalent
- ▶ Compare and contrast characteristics of ionic and covalent compounds
- ▶ Describe how the properties of compounds depend on their bonding
- ▶ Describe how the elements bond by electron transfer (ionic bonding)
- ▶ Describe energy relationships in ionic compounds
- ▶ Predict the formulas of ionic compounds
- ▶ Describe how elements bond by sharing electrons (covalent bonding)
- ▶ Write Lewis dot and dash formulas for molecules and polyatomic ions
- ▶ Recognize exceptions to the octet rule
- ▶ Write formal charges for atoms in covalent structures
- ▶ Describe resonance, and know when to write resonance structures and how to do so
- ▶ Relate the nature of bonding to electronegativity differences

Chemical bonding refers to the attractive forces that hold atoms together in compounds. There are two major classes of bonding. (1) **Ionic bonding** results from the net *transfer* of electrons from one atom or group of atoms to another and the attractive electrostatic interactions among the *cations* and *anions* that are formed. (2) **Covalent bonding** results from the *sharing* of one or more electron pairs between two atoms. These two classes represent two extremes; all bonding between atoms of different elements has at least some degree of both ionic and covalent character. Compounds containing predominantly ionic bonding are called **ionic compounds**. Those that are held together mainly by covalent bonds are called **covalent compounds**. Some general properties associated with ionic and covalent compounds are summarized in the following list.

Ionic Compounds

1. They are solids with high melting points (typically $>400^{\circ}\text{C}$).
2. Many are soluble in polar solvents such as water.
3. Most are insoluble in nonpolar solvents, such as hexane, C_6H_{14} , and carbon tetrachloride, CCl_4 .
4. Ionic liquids conduct electricity well because they contain mobile charged particles (ions).
5. Aqueous solutions conduct electricity well because they contain mobile charged particles (ions).
6. They are often formed between two elements with quite different electronegativities, usually a metal and a nonmetal.

Covalent Compounds

1. They are gases, liquids, or solids with low melting points (typically $<300^{\circ}\text{C}$).
2. Many are insoluble in polar solvents.
3. Most are soluble in nonpolar solvents, such as hexane, C_6H_{14} , and carbon tetrachloride, CCl_4 .
4. Covalent liquids do not conduct electricity.
5. Aqueous solutions are *usually* poor conductors of electricity because most do not contain charged particles.
6. They are often formed between two elements with similar electronegativities, usually nonmetals.

▶ As you study Chapters 7 and 8, keep in mind the periodic similarities that you learned in Chapters 5 and 6. What you learn about the bonding of an element usually applies to the other elements in the same column of the periodic table, with minor variations.

▶ The distinction between polar and nonpolar molecules is discussed in Section 7-10.

▶ As we saw in Section 6-1, aqueous solutions of some covalent compounds do conduct electricity, because they react with water to some extent to form ions.

7-1 Lewis Dot Formulas of Atoms

The number and arrangements of electrons in the outermost shells of atoms determine the chemical and physical properties of the elements as well as the kinds of chemical bonds they form. We write **Lewis formulas** (sometimes called **Lewis dot formulas** or

Table 7-1 Lewis Dot Formulas for Atoms of Representative Elements

Group	1A	2A	3A	4A	5A	6A	7A	8A
Number of electrons in valence shell	1	2	3	4	5	6	7	8 (except He)
Period 1	H·							He :
Period 2	Li·	Be :	B·	C·	N·	O·	F·	Ne :
Period 3	Na·	Mg :	Al·	Si·	P·	S·	Cl·	Ar :
Period 4	K·	Ca :	Ga·	Ge·	As·	Se·	Br·	Kr :
Period 5	Rb·	Sr :	In·	Sn·	Sb·	Te·	I·	Xe :
Period 6	Cs·	Ba :	Tl·	Pb·	Bi·	Po·	At·	Rn :
Period 7	Fr·	Ra :						

► For the Group A elements, the number of valence electrons (dots in the Lewis formula) for the *neutral* atom is equal to the group number. Exception: He (two valence electrons).

Lewis dot representations) as a convenient bookkeeping method for keeping track of these “chemically important electrons.” We now introduce this method for atoms of elements; in our discussion of chemical bonding we will frequently use such formulas for atoms, molecules, and ions.

Chemical bonding involves only the **valence electrons**, which are usually the electrons in the outermost occupied shells. In Lewis dot representations, only the electrons in the outermost occupied *s* and *p* orbitals are shown as dots. Table 7-1 shows Lewis dot formulas for atoms of the representative elements. All elements in a given group have the same outer-shell electron configuration. It is somewhat arbitrary on which side of the atom symbol we write the electron dots. We do, however, represent an electron pair as a pair of dots and an unpaired electron as a single dot. Because of the large numbers of dots, such formulas are not as useful for compounds of the transition metals, lanthanides, and actinides.

► For example, Al has the electron configuration [Ar] 3s²3p¹. The three dots in the Lewis dot formula for Al represent the two *s* electrons (the pair of dots) and the *p* electron (the single dot) beyond the noble gas configuration.

Ionic Bonding

7-2 Formation of Ionic Compounds

The first kind of chemical bonding we will describe is ionic bonding. We recall (see Section 2-2) that an **ion** is an atom or a group of atoms that carries an electrical charge. An ion in which the atom or group of atoms has fewer electrons than protons is positively charged and is called a **cation**; one that has more electrons than protons is negatively charged and is called an **anion**. An ion that consists of only one atom is described as a **monatomic ion**. Examples include the chloride ion, Cl[−], and the magnesium ion, Mg²⁺. An ion that contains more than one atom is called a **polyatomic ion**. Examples include the ammonium ion, NH₄⁺; the hydroxide ion, OH[−]; and the sulfate ion, SO₄^{2−}. The atoms within a polyatomic ion are held to one another by covalent bonds. In this section we shall discuss how ions can be formed from individual atoms; polyatomic ions will be discussed later, along with other covalently bonded species.

Ionic bonding is the attraction of oppositely charged ions (cations and anions) in large numbers to form a solid. Such a solid compound is called an *ionic solid*.

As our previous discussions of ionization energy, electronegativity, and electron affinity would suggest, ionic bonding can occur easily when elements that have low

STOP & THINK

The chemical and physical properties of an ion are quite different from those of the atom from which the ion is derived. For example, an atom of Na and an Na⁺ ion have extremely different chemical properties. It is important to keep track of charges and oxidation states.

Unless otherwise noted, all content on this page is © Cengage Learning.



Charles D. Winters

Freshly cut sodium has a metallic luster. A little while after being cut, the sodium metal surface turns white as it reacts with the air.

electronegativities and low ionization energies (metals) react with elements that have high electronegativities and very negative electron affinities (nonmetals). Many metals are easily *oxidized*—that is, they lose electrons to form cations; and many nonmetals are readily *reduced*—that is, they gain electrons to form anions.

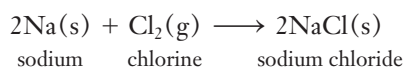
When the electronegativity difference, $\Delta(\text{EN})$, between two elements is large, as between a metal and a nonmetal, the elements are likely to form a compound by ionic bonding (transfer of electrons).

Let's describe some combinations of metals with nonmetals to form ionic compounds.

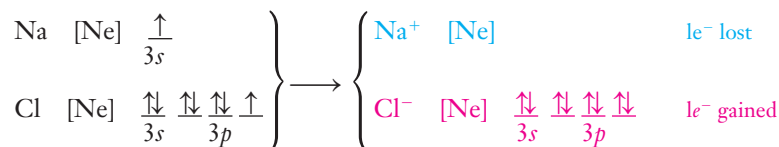
Group 1A Metals (Alkali Metals) and Group 7A Nonmetals (Halogens)

Consider the reaction of sodium (a Group 1A metal) with chlorine (a Group 7A nonmetal). Sodium is a soft silvery metal (mp = 98°C), and chlorine is a yellowish green corrosive gas at room temperature. Both sodium and chlorine react with water; sodium reacts vigorously.

By contrast, sodium chloride is a white solid (mp = 801°C) that dissolves in water with no reaction and with the mild absorption of heat. We can represent the reaction for its formation as



We can understand this reaction better by showing electron configurations for all species. We represent chlorine as individual atoms rather than molecules, for simplicity.



► *Isoelectronic* species have the same number of electrons (see Section 5-5). Some isoelectronic species:

O^{2-}	8 protons	10 electrons
F^-	9 protons	10 electrons
Ne	10 protons	10 electrons
Na^+	11 protons	10 electrons
Mg^{2+}	12 protons	10 electrons

In this reaction, Na atoms lose one electron each to form Na^+ ions, which contain only ten electrons, the same number as the *preceding* noble gas, neon. We say that sodium ions have the noble gas electronic structure of neon: Na^+ is *isoelectronic* with Ne. In contrast, Cl atoms gain one electron each to form Cl^- ions, which contain 18 electrons. This is the same number as the *following* noble gas, argon; Cl^- is *isoelectronic* with Ar. These processes can be represented compactly as



The loss of electrons is *oxidation* (see Section 6-5). Na atoms are *oxidized* to form Na^+ ions. The gain of electrons is *reduction* (see Section 6-5). Cl atoms are *reduced* to form Cl^- ions.

Some ionic compounds. Clockwise from front right: sodium chloride (NaCl , white); copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, blue); nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, green); potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, orange); and cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, red). One mole of each substance is shown.

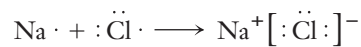


Charles D. Winters

Unless otherwise noted, all content on this page is © Cengage Learning.

Similar observations apply to most ionic compounds formed by reactions between *metals and nonmetals*.

We can use Lewis dot formulas (see Section 7-1) to represent the reaction.



The Na^+ and Cl^- ions can be present only in a 1:1 ratio in the compound sodium chloride, so the formula must be NaCl. We predict the same formula based on the fact that each Na atom can lose only one electron from its outermost occupied shell and each Cl atom needs only one electron to fill completely its outermost *p* orbitals.

The chemical formula NaCl does not explicitly indicate the ionic nature of the compound, only the ratio of ions. Furthermore, values of electronegativities are not always available. We must learn to use the positions of elements in the periodic table and their trends in electronegativity to help recognize when the difference in electronegativity is large enough to favor ionic bonding.

The farther apart *across* the periodic table two elements are, the more ionic their bonding will be.

The greatest difference in electronegativity occurs from the lower left to upper right, so CsF ($\Delta[\text{EN}] = 3.2$) is more ionic than LiI ($\Delta[\text{EN}] = 1.5$).

All the Group 1A metals (Li, Na, K, Rb, Cs) will react with the Group 7A elements (F, Cl, Br, I) to form ionic compounds of the same general formula, MX. All the resulting ions, M^+ and X^- , have noble gas configurations. Once we understand the bonding of one member of a group (column) in the periodic table, we know a great deal about the others in the family. Combining each of the five common alkali metals with each of the four common halogens gives $5 \times 4 = 20$ possible compounds. The discussion of NaCl presented here applies also to the other 19 such compounds.

The collection of isolated positive and negative ions occurs at a higher energy than the elements from which they are formed. The ion formation alone is not sufficient to account for the formation of ionic compounds. Some other favorable factor must account for the observed stability of these compounds. Because of the opposite charges on Na^+ and Cl^- , an attractive force is developed. According to Coulomb's Law, the force of attraction, *F*, between two oppositely charged particles of charge magnitudes q^+ and q^- is directly proportional to the product of the charges and inversely proportional to the square of the distance separating their centers, *d*.

$$\text{Coulomb's Law is } F \propto \frac{q^+ q^-}{d^2}.$$

Thus, the greater the charges on the ions and the smaller the ions are, the stronger the resulting ionic bonding. Of course, ions with the same charge repel each other, so the distances separating the ions in ionic solids are those at which the attractions exceed the repulsions by the greatest amount.

The energy associated with the attraction of separated gaseous positive and negative ions to form an ionic solid is the *crystal lattice energy* of the solid. For NaCl, this energy is -789 kJ/mol ; that is, one mole of NaCl solid is 789 kJ lower in energy (*more stable*) than one mole of isolated Na^+ ions and one mole of isolated Cl^- ions. We could also say that it would require 789 kJ of energy to separate one mole of NaCl solid into isolated gaseous ions. The stability of ionic compounds is thus due to the interplay of the energy cost of ion formation and the energy repaid by the crystal lattice energy. The best trade-off usually comes when the monatomic ions of representative elements have noble gas configurations. For more on these ideas, see the Enrichment feature "Introduction to Energy Relationships in Ionic Bonding" on page 256.

► The noble gases and hydrogen are excluded from this generalization.

► Formulas for some of these are

LiF	LiCl	LiBr	LiI
NaF	NaCl	NaBr	NaI
KF	KCl	KBr	KI

► The symbol $\propto$ means "is proportional to."

► Although the common name for NaCl is "salt," many chemists use the term salt in a more generic way to refer to ionic compounds.

Unless otherwise noted, all content on this page is © Cengage Learning.

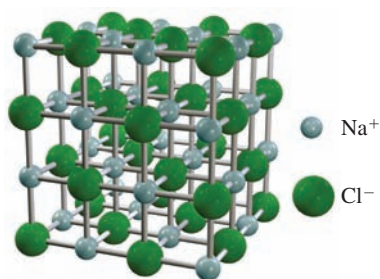


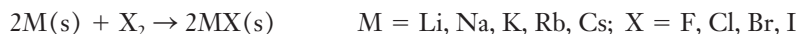
Figure 7-1 A representation of the crystal structure of NaCl. Each Cl^- ion (green) is surrounded by six sodium ions, and each Na^+ ion (gray) is surrounded by six chloride ions. Any NaCl crystal includes billions of ions in the pattern shown. Adjacent ions actually are in contact with one another; in this drawing, the structure has been expanded to show the spatial arrangement of ions. The lines *do not* represent covalent bonds. Compare with Figure 2-2, a space-filling drawing of the NaCl structure.

▶ Although the oxides of the other Group 1A metals are prepared by different methods, similar descriptions apply to compounds between the Group 1A metals (Li, Na, K, Rb, Cs) and the Group 6A nonmetals (O, S, Se, Te, Po).

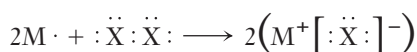
▶ Each Li atom has $1e^-$ in its valence shell, one more e^- than a noble gas configuration, [He]. Each O atom has $6e^-$ in its valence shell and needs $2e^-$ more to attain a noble gas configuration [Ne]. The Li^+ ions are formed by oxidation of Li atoms, and the O^{2-} ions are formed by reduction of O atoms.

The structure of common table salt, sodium chloride (NaCl), is shown in Figure 7-1. Like other simple ionic compounds, NaCl(s) exists in a regular, extended array of positive and negative ions, Na^+ and Cl^- . Distinct molecules of solid ionic substances do not exist, so we must refer to *formula units* (see Section 2-2) instead of molecules. The forces that hold all the particles together in an ionic solid are quite strong. This explains why such substances have quite high melting and boiling points (a topic that we will discuss more fully in Chapter 13). When an ionic compound is melted or dissolved in water, its charged particles are free to move in an electric field, so such a liquid shows high electrical conductivity (Section 6-1, Part 1).

We can represent the general reaction of the 1A metals with the 7A elements as follows:

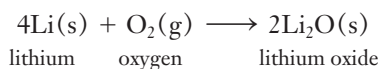


The Lewis dot representation for the generalized reaction is

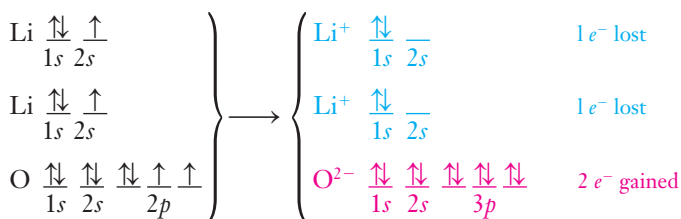


Group 1A Metals (Alkali Metals) and Group 6A Nonmetals

Next, consider the reaction of lithium (Group 1A) with oxygen (Group 6A) to form lithium oxide, a solid ionic compound (mp > 1700°C). We may represent the reaction as



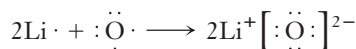
The formula for lithium oxide, Li_2O , indicates that two atoms of lithium combine with one atom of oxygen. If we examine the structures of the atoms before reaction, we can see the reason for this ratio.



In a compact representation,



The Lewis dot formulas for the atoms and ions are



Lithium ions, Li^+ , are isoelectronic with helium atoms ($2e^-$). Oxide ions, O^{2-} , are isoelectronic with neon atoms ($10e^-$).

The very small size of the Li^+ ion gives it a much higher *charge density* (ratio of charge to size) than that of the larger Na^+ ion (see Figure 5-4). Similarly, the O^{2-} ion is smaller than the Cl^- ion, so its smaller size and double negative charge give it a much higher charge density. These more concentrated charges and smaller sizes bring the Li^+ and O^{2-} ions closer together in Li_2O than the Na^+ and Cl^- ions are in NaCl. Consequently, the q^+q^- product in the numerator of Coulomb's Law is greater in Li_2O , and the d^2 term in the denominator is smaller. The net result is that the ionic bonding is much stronger (the lattice energy is much more negative) in Li_2O than in NaCl. This is consistent with the higher melting temperature of Li_2O (> 1700°C) compared to NaCl (801°C).



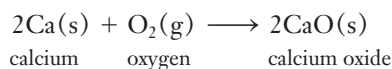
Lithium is a metal, as the shiny surface of freshly cut Li shows. Where it has been exposed to air, the surface is covered with lithium oxide.

Charles Steele

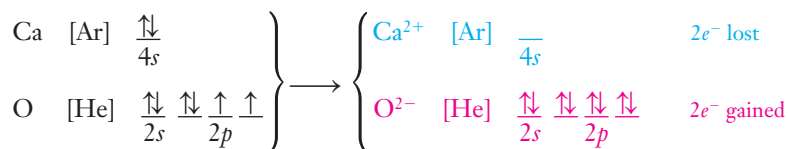
Unless otherwise noted, all content on this page is © Cengage Learning.

Group 2A Metals (Alkaline Earth Metals) and Group 6A Nonmetals

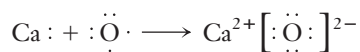
As our final illustration of ionic bonding, consider the reaction of calcium (Group 2A) with oxygen (Group 6A). This reaction forms calcium oxide, a white solid ionic compound with a very high melting point, 2580°C.



Again, we show the electronic structure of the atoms and ions, representing the inner electrons by the symbol of the preceding noble gas.



The Lewis dot notation for the reacting atoms and the resulting ions is

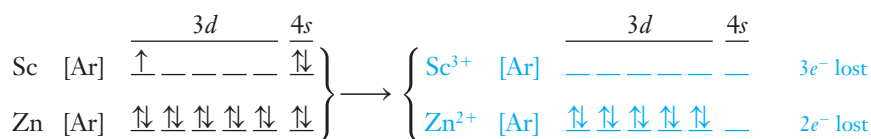


Calcium ions, Ca^{2+} , are isoelectronic with argon ($18e^-$), the preceding noble gas. Oxide ions, O^{2-} , are isoelectronic with neon ($10e^-$), the following noble gas.

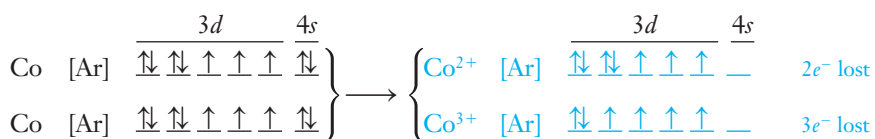
Ca^{2+} is about the same size as Na^+ (see Figure 5-4) but carries twice the charge, so its charge density is higher. Because the attraction between the two small, highly charged ions Ca^{2+} and O^{2-} is quite high, the ionic bonding is very strong, accounting for the very high melting point of CaO , 2580°C.

d-Transition Metal Ions

Electron configurations of the *d*-transition metal atoms include the *s* electrons in the outermost occupied shell and the *d* electrons one energy level lower (e.g., $3d4s$ for the first transition series in Period 4). The outer *s* electrons lie outside the *d* electrons and are *always* the first ones lost when transition metals form simple ions. In the first transition series, scandium and zinc each form only one type of cation. Scandium loses its two $4s$ electrons and its only $3d$ electron to form Sc^{3+} . Zinc loses its two $4s$ electrons to form Zn^{2+} .



Most other $3d$ -transition metals can form at least two differently charged cations in their compounds. For example, cobalt commonly forms Co^{2+} and Co^{3+} ions.



Binary Ionic Compounds: A Summary

Table 7-2 summarizes the general formulas of binary ionic compounds formed by the representative elements. “M” represents metals, and “X” represents nonmetals from the indicated groups. In these examples of ionic bonding, each of the metal atoms has lost one, two, or

► This discussion also applies to other ionic compounds between any Group 2A metal (Be, Mg, Ca, Sr, Ba) and any Group 6A nonmetal (O, S, Se, Te).

► Chemists do not ordinarily represent transition metals or their ions as Lewis dot formulas.



Many transition metal ions are highly colored. These flasks contain (left to right), aqueous solutions of $\text{Fe}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, and $\text{Zn}(\text{NO}_3)_2$. Colorless Zn^{2+} ions differ from the others by having completely filled $3d$ orbitals.

Charles D. Winters

► **Binary compounds** contain two elements.

Table 7-2 Simple Binary Ionic Compounds

Metal		Nonmetal		General Formula	Ions Present	Example	mp (°C)
1A*	+	7A	→	MX	(M ⁺ , X ⁻)	LiBr	547
2A	+	7A	→	MX ₂	(M ²⁺ , 2X ⁻)	MgCl ₂	708
3A	+	7A	→	MX ₃	(M ³⁺ , 3X ⁻)	GaF ₃	800 (subl)
1A [†]	+	6A	→	M ₂ X	(2M ⁺ , X ²⁻)	Li ₂ O	>1700
2A	+	6A	→	MX	(M ²⁺ , X ²⁻)	CaO	2580
3A	+	6A	→	M ₂ X ₃	(2M ³⁺ , 3X ²⁻)	Al ₂ O ₃	2045
1A*	+	5A	→	M ₃ X	(3M ⁺ , X ³⁻)	Li ₃ N	840
2A	+	5A	→	M ₃ X ₂	(3M ²⁺ , 2X ³⁻)	Ca ₃ P ₂	1600
3A	+	5A	→	MX	(M ³⁺ , X ³⁻)	AlP	

*Hydrogen is a nonmetal. All binary compounds of hydrogen are covalent, except for certain metal hydrides such as NaH and CaH₂, which contain hydride, H⁻, ions.

[†]As we saw in Section 5-9, the metals in Groups 1A and 2A also commonly form peroxides (containing the O₂²⁻ ion) or superoxides (containing the O₂⁻ ion) (see Table 5-5). The peroxide and superoxide ions contain atoms that are covalently bonded to one another.

► “subl” stands for sublimates, that is, the solid transforms directly to the gas phase without forming a liquid state.

three electrons, and each of the nonmetal atoms has gained one, two, or three electrons. *Simple (monatomic) ions rarely have charges greater than 3+ or 3-.* Ions with greater charges interact strongly with the electron clouds of other ions. The electron clouds become very distorted, resulting in considerable covalent character in the bonds. Distinct molecules of solid ionic substances do not exist. The sum of the attractive forces of all the interactions in an ionic solid is substantial. Therefore, binary ionic compounds have high melting and boiling points.

► The distortion of the electron cloud of an anion by a small, highly charged cation is called *polarization*.

All common monatomic anions have noble gas configurations. Most monatomic cations of the representative elements (A groups) have noble gas configurations. The *d*- and *f*-transition elements form many compounds that are essentially ionic in character. Most *d*- and *f*-transition metal cations do not have noble gas configurations.

ENRICHMENT

Introduction to Energy Relationships in Ionic Bonding

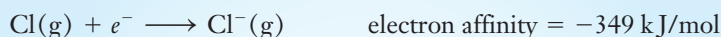
The following discussion may help you to understand why ionic bonding occurs between elements with low ionization energies and those with high electronegativities. There is a general tendency in nature to achieve stability. One way to do this is by lowering potential energy; *lower* energies generally represent *more stable* arrangements.

Let's use energy relationships to describe why the ionic solid NaCl is more stable than a mixture of individual Na and Cl atoms. Consider a gaseous mixture of one mole of sodium atoms and one mole of chlorine atoms, Na(g) + Cl(g). The energy change associated with the loss of one mole of electrons by one mole of Na atoms to form one mole of Na⁺ ions (Step 1 in Figure 7-2) is given by the *first ionization energy* of Na (see Section 5-3).



This is a positive value, so the mixture Na⁺(g) + e⁻ + Cl(g) is 496 kJ/mol higher in energy than the original mixture of atoms (the mixture Na⁺ + e⁻ + Cl is *less stable* than the mixture of atoms).

The energy change for the gain of one mole of electrons by one mole of Cl atoms to form one mole of Cl^- ions (Step 2) is given by the *electron affinity* of Cl (see Section 5-4).



This negative value, -349 kJ/mol , lowers the energy of the mixture, but the mixture of separated ions, $\text{Na}^+ + \text{Cl}^-$, is still *higher* in energy (*less stable*) by $(496 - 349) \text{ kJ/mol} = 147 \text{ kJ/mol}$ than the original mixture of atoms (the red arrow in Figure 7-2). Thus, just the formation of ions does not explain why the process occurs. The strong attractive force between ions of opposite charge draws the ions together into the regular array shown in Figure 7-1. The energy associated with this attraction (Step 3) is the *crystal lattice energy* of NaCl, -789 kJ/mol .



The crystal (solid) formation thus further *lowers* the energy to $(147 - 789) \text{ kJ/mol} = -642 \text{ kJ/mol}$. The overall result is that one mole of NaCl(s) is 642 kJ/mol lower in energy (more stable) than the original mixture of atoms (the blue arrow in Figure 7-2). The very large electrostatic stabilization due to the attraction of the ionic charges (Step 3) is a major driving force for the formation of ionic compounds.

In this discussion we have not taken into account the fact that sodium is a solid metal or that chlorine gas exists as diatomic molecules. The additional energy changes involved when these are changed to gaseous Na and Cl atoms, respectively, are small enough that the overall energy change starting from Na(s) and $\text{Cl}_2(\text{g})$ is still negative.

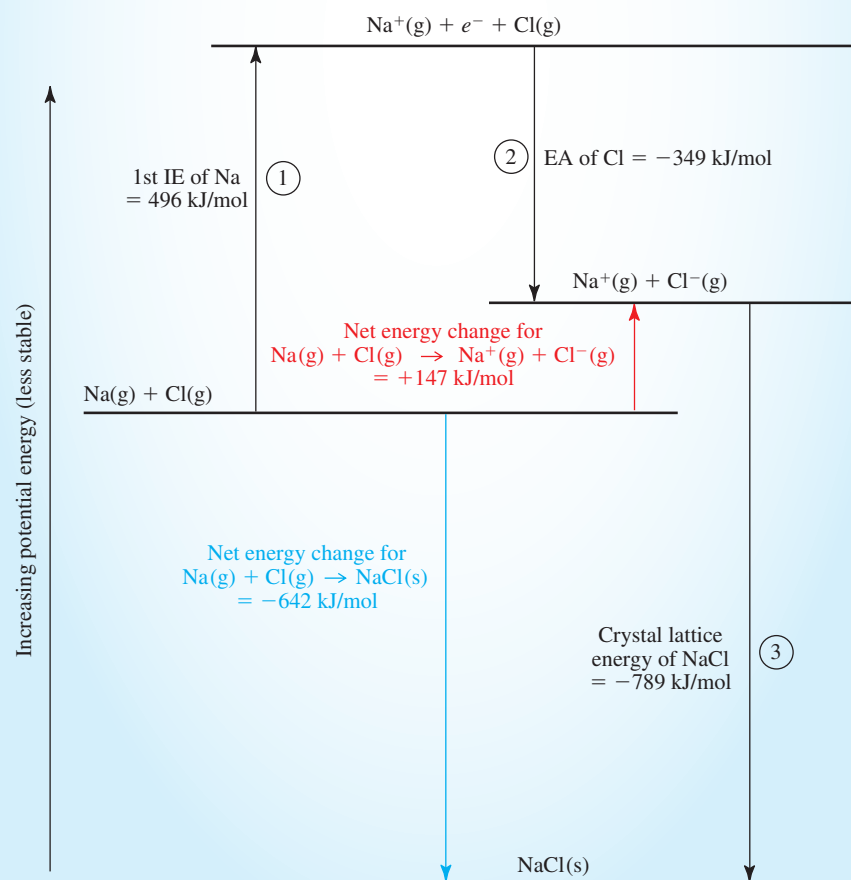
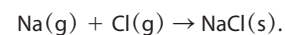
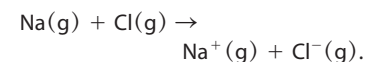


Figure 7-2 A schematic representation of the energy changes that accompany the process



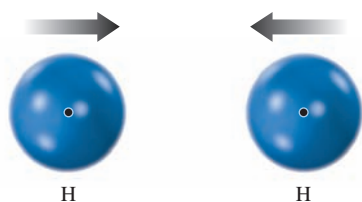
The red arrow represents the *positive* energy change (unfavorable) for the process of ion formation,



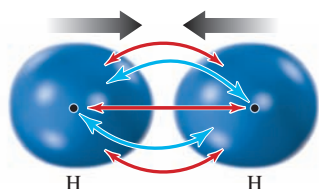
The blue arrow represents the *negative* energy change (favorable) for the overall process, including the formation of the ionic solid.

Unless otherwise noted, all content on this page is © Cengage Learning.

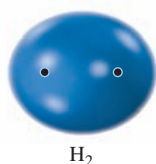
Covalent Bonding



A Two hydrogen atoms separated by a large distance



B As the atoms approach each other, the electron of each atom is attracted by the positively charged nucleus of the other atom (blue arrows), so the electron density begins to shift. At the same time, the electron clouds of the two atoms repel one another, and so do the nuclei of the two atoms (red arrows).



C The two electrons can both be in the region where the two $1s$ orbitals overlap; the electron density is highest in the region between the nuclei of the two atoms.

Figure 7-3 A representation of the formation of a covalent bond between two hydrogen atoms. The position of each positively charged nucleus is represented by a black dot.

Ionic bonding cannot result from a reaction between two atoms with similar electronegativities, because their electronegativity difference is not great enough for electron transfer to take place. Instead, these reactions, typically between nonmetals, result in *covalent bonding*.

A **covalent bond** is formed when two atoms share one or more pairs of electrons. Covalent bonding occurs when the electronegativity difference, $\Delta(\text{EN})$, between elements (atoms) is zero or relatively small.

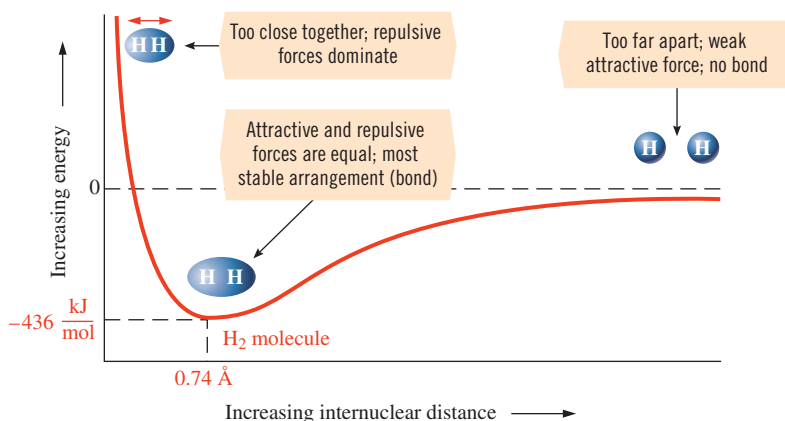
In predominantly covalent compounds the bonds between atoms *within* a molecule (*intramolecular bonds*) are relatively strong, but the forces of attraction *between* molecules (*intermolecular forces*) are relatively weak. As a result, covalent compounds have lower melting and boiling points than ionic compounds. The relation of bonding types to physical properties of liquids and solids will be developed more fully in Chapter 13.

7-3 Formation of Covalent Bonds

Let's look at the simplest case of covalent bonding, the reaction of two hydrogen atoms to form the diatomic molecule H_2 . As you recall, an isolated hydrogen atom has the ground state electron configuration $1s^1$, with the probability density for this one electron spherically distributed about the hydrogen nucleus (Figure 7-3a). As two hydrogen atoms approach each other from large distances, the electron of each hydrogen atom is attracted by the nucleus of the *other* hydrogen atom as well as by its own nucleus (see Figure 7-3b). If these two electrons have opposite spins so that they can occupy the same region (orbital), both electrons can now preferentially occupy the region *between* the two nuclei (see Figure 7-3c), where they are strongly attracted by *both* nuclei. A pair of electrons is *shared* between the two hydrogen atoms, and a single covalent bond is formed. We say that the $1s$ orbitals *overlap* so that both electrons are now in the orbitals of both hydrogen atoms. The closer together the atoms come, the more nearly this is true. In that sense, each hydrogen atom then has the helium configuration $1s^2$.

The bonded atoms are at lower energy (more stable) than the separated atoms. This is shown in the plot of energy versus distance in Figure 7-4. As the two atoms get closer together, however, the two nuclei, being positively charged, exert an increasing repulsion on each other. At some distance, a minimum energy, -436 kJ/mol , is reached; it corresponds to the most stable arrangement and occurs at $0.74 \text{ \AA}$, the actual distance between two hydrogen nuclei in an H_2 molecule. At distances greater than this, the attractive forces exceed the repulsive ones, so the atoms are drawn closer together. At smaller separations, repulsive forces increase more rapidly than attractive ones, so repulsive forces dominate and the arrangement is less stable.

Figure 7-4 The potential energy of the H_2 molecule as a function of the distance between the two nuclei. The lowest point in the curve, -436 kJ/mol , corresponds to the internuclear distance actually observed in the H_2 molecule, $0.74 \text{ \AA}$. At distances longer than this, attractive forces dominate; at distances shorter than this, repulsive forces dominate. (The minimum potential energy, -436 kJ/mol , corresponds to the value of $-7.23 \times 10^{-19} \text{ J/H}_2$ molecule.) Energy is compared with that of two separated hydrogen atoms.



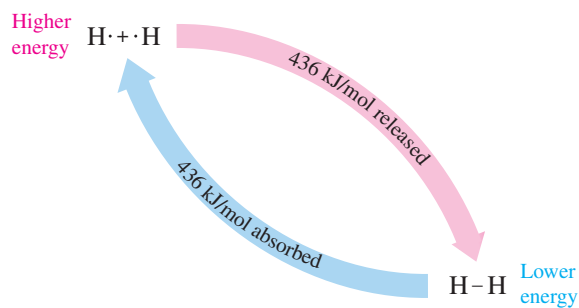
Unless otherwise noted, all content on this page is © Cengage Learning.

Other pairs of nonmetal atoms share electron pairs to form covalent bonds. The result of this sharing is that each atom attains a more stable electron configuration—frequently the same as that of the nearest noble gas. This results in a more stable arrangement for the bonded atoms. (This is discussed in Section 7-6.) Most covalent bonds involve sharing of two, four, or six electrons—that is, one, two, or three *pairs* of electrons. Two atoms form a **single covalent bond** when they share one pair of electrons, a **double covalent bond** when they share two electron pairs, and a **triple covalent bond** when they share three electron pairs. These are usually called simply *single*, *double*, and *triple* bonds. Covalent bonds that involve sharing of one and three electrons are known but are relatively rare.

In our discussion, we have described how covalent bonds form by the *overlap* of two atomic orbitals. This is the essence of the *valence bond theory*, which we will describe in more detail in the next chapter. Another description, the *molecular orbital theory*, is discussed in Chapter 9. For the rest of this chapter, we concentrate on the *number* of electron pairs shared and defer the discussion of *which* orbitals are involved in the sharing until the next chapter.

7-4 Bond Lengths and Bond Energies

We have seen that for any covalent bond there is some internuclear distance at which the attractive and repulsive forces balance and the bond is most stable; this distance is called the **bond length** of that covalent bond. At that distance, the combination of bonded atoms is more stable than the separated atoms by some energy; this energy difference is called the **bond dissociation energy**, or just the **bond energy**. This can be viewed as the stabilization of the bond compared to the separated atoms. It can also be described as the energy that must be supplied to separate the atoms, breaking the covalent bond.



Similar bonds between the same pairs of atoms usually have similar bond lengths and bond energies. Thus, we can develop tables of typical bond energies (Table 7-3) and bond lengths (Table 7-4) for each type of covalent bond.

Let's compare some typical carbon–carbon bond lengths and energies:

	Single Bond	Double Bond	Triple Bond
Bond length (Å)	1.54 Å	1.34 Å	1.21 Å
Bond energy (kJ/mol)	346	602	835

► Note that a C=C double bond is not twice as strong as a single bond. Similarly, a triple bond is not three times as strong as a single bond.

Table 7-3 Selected Average Bond Dissociation Energies (kJ/mol)

	Single Bonds						Double Bonds	Triple Bonds
	H	C	N	O	F	S		
H	436	413	391	463	563	347		
C		346	305	358	485	272	C=C 602	C≡C 835
N			163	201	283	—	C=N 615	C≡N 887
O				146	190	—	C=O 732 (except	C≡O 1072
F					155	284	in CO ₂ , where it	
S						226	is 799)	

Table 7-4 Selected Average Bond Lengths (Å)

	Single Bonds						Double Bonds	Triple Bonds
	H	C	N	O	F	S		
H	0.74	1.10	0.98	0.94	0.92	1.32		
C		1.54	1.47	1.43	1.41	1.81	C=C 1.34	C≡C 1.21
N			1.40	1.36	1.34	1.74	C=N 1.27	C≡N 1.15
O				1.32	1.30	1.70	C=O 1.22	C≡O 1.13
F					1.28	1.68		
S						2.08		

► Although multiple bonds are stronger than single bonds, they are often more reactive, especially for C—C double and triple bonds.

We see that the more bonds there are between atoms of the same two elements (i.e., the more electron pairs are shared), the closer together those atoms are (the shorter the bond length is) and the harder it is to break the bonding (increasing bond energy). Similar patterns can be seen for any other pairs of elements. Bond dissociation energies will be discussed in more rigorous detail in Section 15-9.

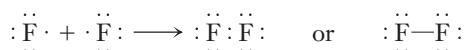
7-5 Lewis Formulas for Molecules and Polyatomic Ions

In Sections 7-1 and 7-2 we drew *Lewis dot formulas* for atoms and monatomic ions. We can use Lewis formulas to show the *valence electrons* in molecules and polyatomic ions.

In a Lewis formula, we represent a covalent bond by writing *each shared electron pair* either as a pair of two dots between the two atom symbols or as a dash connecting them. Thus, the formation of H₂ from H atoms could be represented as



where the dash represents a single bond. Similarly, the combination of two fluorine atoms to form a molecule of fluorine, F₂, can be shown as



The formation of a hydrogen fluoride molecule, HF, from a hydrogen atom and a fluorine atom can be shown as

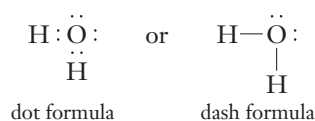


► The bonding in the other halogens, Cl₂, Br₂, and I₂, is analogous to that in F₂.

► The bonding in gaseous HCl, HBr, and HI is analogous to that in HF.

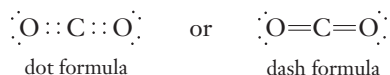
Unless otherwise noted, all content on this page is © Cengage Learning.

A water molecule can be represented by either of the following diagrams.



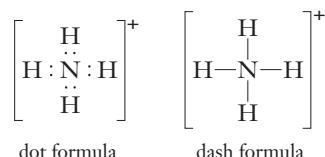
An H_2O molecule has two shared electron pairs, that is, two single covalent bonds. The O atom also has two unshared pairs.

In *dash formulas*, a shared pair of electrons is indicated by a dash. The following diagrams show the two *double* bonds in carbon dioxide and its Lewis formula.



A CO_2 molecule has four shared electron pairs in two double bonds. The central atom (C) has no unshared pairs.

The covalent bonds in a polyatomic ion can be represented in the same way. The Lewis formula for the ammonium ion, NH_4^+ , shows only eight electrons, even though the N atom has five electrons in its valence shell and each H atom has one, for a total of $5 + 4(1) = 9$ electrons. The NH_4^+ ion, with a charge of $1+$, has one fewer electron than the original atoms.



The writing of Lewis formulas is an electron bookkeeping method that is useful as a first approximation to suggest bonding schemes. It is important to remember that Lewis dot formulas only show the number of valence electrons, the number and kinds of bonds, and the order in which the atoms are connected. *They are not intended to show the three-dimensional shapes of molecules and polyatomic ions.* We will see in Chapter 8, however, that the three-dimensional geometry of a molecule can be predicted from its Lewis formula.

7-6 Writing Lewis Formulas: The Octet Rule

Representative elements usually attain stable noble gas electron configurations when they share electrons. In the water molecule eight electrons are in the outer shell of the O atom, and it has the neon electron configuration; two electrons are in the valence shell of each H atom, and each has the helium electron configuration. Likewise, the C and O of CO_2 and the N of NH_3 and the NH_4^+ ion each have a share in eight electrons in their outer shells. The H atoms in NH_3 and NH_4^+ each share two electrons. Many Lewis formulas are based on the idea that

in *most* of their compounds, the representative elements achieve noble gas configurations.

This statement is usually called the **octet rule** because the noble gas configurations have $8e^-$ in their outermost shells (except for He, which has $2e^-$).

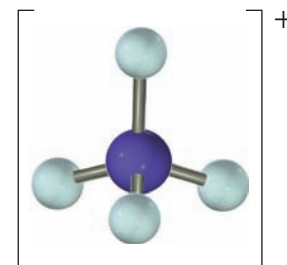
For now, we restrict our discussion to compounds of the *representative elements*. The octet rule alone does not let us write Lewis formulas. We still must decide how to place the electrons around the bonded atoms—that is, how many of the available valence electrons are present as **bonding pairs** (shared) and how many are as **unshared pairs** (associated with only one atom). A pair of unshared electrons in the same orbital is called a **lone pair**. A simple mathematical relationship is helpful here:

▶ In H_2O , two of the six valence electrons of an oxygen atom are used in covalent bonding; the one valence electron of each hydrogen atom is used in covalent bonding.

▶ In CO_2 , the four valence electrons of a carbon atom are used in covalent bonding; two of the six valence electrons of each oxygen atom are used in covalent bonding.

▶ A polyatomic ion is an ion that contains more than one atom.

▶ The NH_3 molecule, like the NH_4^+ ion, has eight valence electrons about the N atom. As we will see in Chapter 8, the three-dimensional shapes of the NH_3 molecule and the NH_4^+ ion are:



▶ In some compounds, the central atom does not achieve a noble gas configuration. Such exceptions to the octet rule are discussed in Section 7-8.

▶ The representative elements are those in the A groups of the periodic table.

$$S = N - A$$

where S is the total number of electrons *shared* in the molecule or polyatomic ion.

N is the total number of valence shell electrons *needed* by all the atoms in the molecule or ion to achieve noble gas configurations ($N = 8 \times$ number of atoms that are not H, plus $2 \times$ number of H atoms).

A is the total number of electrons *available* in the valence shells of all of the (representative) atoms. This is equal to the sum of their periodic group numbers. If necessary, adjust A for ionic charges. To do this, we add electrons to account for negative charges and subtract electrons to account for positive charges.

Let's see how this relationship applies to some species whose Lewis formulas we have already shown.

For F_2 ,

$$N = 2 \times 8 \text{ (for two F atoms)} = 16e^- \text{ needed}$$

$$A = 2 \times 7 \text{ (for two F atoms)} = 14e^- \text{ available}$$

$$S = N - A = 16 - 14 = 2e^- \text{ shared}$$



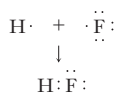
The Lewis formula for F_2 shows 14 valence electrons total, with $2e^-$ shared in a single bond. An alternative way of approaching this is to focus on the unpaired electrons on each atom and pair them to form a covalent bond.

For HF,

$$N = 1 \times 2 \text{ (for one H atom)} + 1 \times 8 \text{ (for one F atom)} = 10e^- \text{ needed}$$

$$A = 1 \times 1 \text{ (for one H atom)} + 1 \times 7 \text{ (for one F atom)} = 8e^- \text{ available}$$

$$S = N - A = 10 - 8 = 2e^- \text{ shared}$$



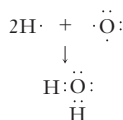
The Lewis formula for HF shows 8 valence electrons total, with $2e^-$ shared in a single bond. Once again, focusing on the unpaired electrons and pairing them to form a covalent bond gets the same answer.

For H_2O ,

$$N = 2 \times 2 \text{ (for two H atoms)} + 1 \times 8 \text{ (for one O atom)} = 12e^- \text{ needed}$$

$$A = 2 \times 1 \text{ (for two H atoms)} + 1 \times 6 \text{ (for one O atom)} = 8e^- \text{ available}$$

$$S = N - A = 12 - 8 = 4e^- \text{ shared}$$



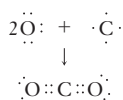
The Lewis formula for H_2O shows 8 valence electrons total, with a total of $4e^-$ shared, $2e^-$ in each single bond. Once again, focusing on the unpaired electrons and pairing them to form two covalent bonds gets the same answer.

For CO_2 ,

$$N = 1 \times 8 \text{ (for one C atom)} + 2 \times 8 \text{ (for two O atoms)} = 24e^- \text{ needed}$$

$$A = 1 \times 4 \text{ (for one C atom)} + 2 \times 6 \text{ (for two O atoms)} = 16e^- \text{ available}$$

$$S = N - A = 24 - 16 = 8e^- \text{ shared}$$



The Lewis formula for CO_2 shows 16 valence electrons total, with a total of $8e^-$ shared, $4e^-$ in each double bond. For this example, pairing the unpaired electrons is not quite as obvious. The margin diagram shows the O atom with all electrons paired. But if you unpair the electrons on O as shown for the water example above, it becomes more clear that the two unpaired electrons on each oxygen atom can pair with two of the unpaired electrons on each carbon to make two $C=O$ double bonds. Then check to verify that each O and C atom has an octet of electrons in the final Lewis dot structure.

For NH_4^+ ,

$$N = 1 \times 8 \text{ (for one N atom)} + 4 \times 2 \text{ (for four H atoms)} = 16e^- \text{ needed}$$

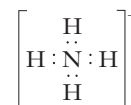
$$A = 1 \times 5 \text{ (for one N atom)} + 4 \times 1 \text{ (for four H atoms)} - 1 \text{ (for 1+ charge)} = 8e^- \text{ available}$$

$$S = N - A = 16 - 8 = 8e^- \text{ shared}$$

The Lewis formula for NH_4^+ shows 8 valence electrons total, with all $8e^-$ shared, $2e^-$ in each single bond.

The following general steps describe the use of the $S = N - A$ relationship in constructing dot formulas for molecules and polyatomic ions.

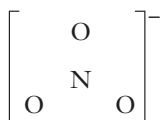
► The 1+ ionic charge is due to a *deficiency* of one e^- relative to the neutral atoms.



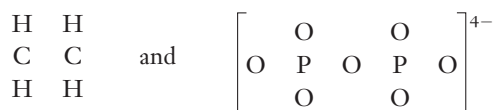
A Guide to Writing Lewis Formulas

1. Select a reasonable (symmetrical) “skeleton” for the molecule or polyatomic ion.

- The *least electronegative element* is usually the central element, except that H is never the central element, because it forms only one bond. The least electronegative element is usually the one that needs the most electrons to fill its octet. Example: CS_2 has the skeleton $\text{S} - \text{C} - \text{S}$.
- Carbon bonds to two, three, or four atoms, but *never* more than four. Nitrogen bonds to one (rarely), two, three (most commonly), or four atoms. Oxygen bonds to one, two (most commonly), or three atoms.
- Oxygen atoms do not bond to each other except in (1) O_2 and O_3 molecules; (2) hydrogen peroxide, H_2O_2 , and its derivatives, the peroxides, which contain the O_2^{2-} group; and (3) the rare superoxides, which contain the O_2^- group.
Example: The nitrate ion, NO_3^- , has the skeleton



- In *ternary oxoacids*, hydrogen usually bonds to an O atom, *not* to the central atom. Example: Nitrous acid, HNO_2 , has the skeleton $\text{H} - \text{O} - \text{N} - \text{O}$. There are a few exceptions to this guideline, such as H_3PO_3 and H_3PO_2 .
- For ions or molecules that have more than one central atom, the most symmetrical skeletons possible are used. Examples: C_2H_4 and $\text{P}_2\text{O}_7^{4-}$ have the following skeletons:



► A ternary oxoacid contains *three* elements—H, O, and another element, often a nonmetal.

2. Calculate N , the number of valence (outer) shell electrons needed by all atoms in the molecule or ion to achieve noble gas configurations. Examples:

For PF_3 ,

$$N = 1 \times 8 \text{ (P atom)} + 3 \times 8 \text{ (F atoms)} = 32e^- \text{ needed}$$

For CH_3OH ,

$$N = 1 \times 8 \text{ (C atom)} + 4 \times 2 \text{ (H atoms)} + 1 \times 8 \text{ (O atom)} = 24e^- \text{ needed}$$

For NO_3^- ,

$$N = 1 \times 8 \text{ (N atom)} + 3 \times 8 \text{ (O atoms)} = 32e^- \text{ needed}$$

► For compounds containing only representative elements, N is equal to $8 \times$ number of atoms that are *not* H, plus $2 \times$ number of H atoms.

► For the representative elements, the number of valence shell electrons in an atom is equal to its periodic group number. Exceptions: 1 for an H atom and 2 for He.

Calculate A , the number of electrons available in the valence (outer) shells of all the atoms. For negatively charged ions, add to this total the number of electrons equal to the charge on the anion; for positively charged ions, subtract the number of electrons equal to the charge on the cation. Examples:

For PF_3 ,

$$A = 1 \times 5 \text{ (P atom)} + 3 \times 7 \text{ (F atoms)} = 26e^- \text{ available}$$

For CH_3OH ,

$$A = 1 \times 4 \text{ (C atom)} + 4 \times 1 \text{ (H atoms)} + 1 \times 6 \text{ (O atom)} = 14e^- \text{ available}$$

For NO_3^- ,

$$A = 1 \times 5 \text{ (N atom)} + 3 \times 6 \text{ (O atoms)} + 1 \text{ (for } 1- \text{ charge)} = 5 + 18 + 1 = 24e^- \text{ available}$$

Calculate S , total number of electrons shared in the molecule or ion, using the relationship $S = N - A$. Examples:

For PF_3 ,

$$S = N - A = 32 - 26 = 6 \text{ electrons shared (3 pairs of } e^- \text{ shared)}$$

For CH_3OH ,

$$S = N - A = 24 - 14 = 10 \text{ electrons shared (5 pairs of } e^- \text{ shared)}$$

For NO_3^- ,

$$S = N - A = 32 - 24 = 8e^- \text{ shared (4 pairs of } e^- \text{ shared)}$$

► C, N, and O often form double and triple bonds. S can form double bonds with C, N, and O.

► Formulas are sometimes written to give clues about which atoms are bonded together. In this format, the H atoms are bonded to the atom preceding them; in CH_3OH the first three H atoms are bonded to C, and the last H atom is bonded to O. Unfortunately, oxoacids rarely follow this guideline. In H_2SO_4 , HNO_3 , and H_3PO_4 , the hydrogen atoms are attached to the oxygen atoms.

3. Place the S electrons into the skeleton as shared pairs. Use double and triple bonds only when necessary. Lewis formulas may be shown as either dot formulas or dash formulas.

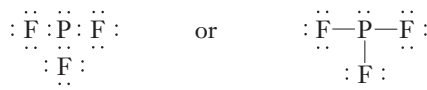
Formula	Skeleton	Dot Formula ("bonds" in place, but incomplete)	Dash Formula ("bonds" in place, but incomplete)
PF_3	$\begin{array}{c} \text{F} \quad \text{P} \quad \text{F} \\ \text{F} \end{array}$	$\begin{array}{c} \text{F} : \text{P} : \text{F} \\ \text{F} \end{array}$	$\begin{array}{c} \text{F}-\text{P}-\text{F} \\ \text{F} \end{array}$
CH_3OH	$\begin{array}{c} \text{H} \\ \text{H} \quad \text{C} \quad \text{O} \quad \text{H} \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \text{H} : \text{C} : \text{O} : \text{H} \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \text{H}-\text{C}-\text{O}-\text{H} \\ \text{H} \end{array}$
NO_3^-	$\left[\begin{array}{ccc} & \text{O} & \\ \text{O} & \text{N} & \text{O} \end{array} \right]^-$	$\left[\begin{array}{ccc} & \text{O} & \\ \text{O} & \text{N} & \text{O} \end{array} \right]^-$	$\left[\begin{array}{ccc} & \text{O} & \\ \text{O} & \text{N} & \text{O} \end{array} \right]^-$

STOP & THINK

A very common error in writing Lewis formulas is showing the wrong total number (A) of valence electrons. Always make a final check to be sure that the Lewis formula you write shows the number of valence electrons you calculated as A .

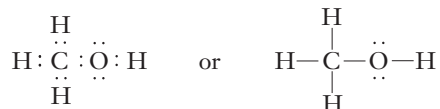
4. Place the additional electrons into the skeleton as *unshared (lone) pairs* to fill the octet of every A group element (except H, which can share only $2e^-$). Check that the total number of valence electrons is equal to A , from Step 2. Examples:

For PF_3 ,



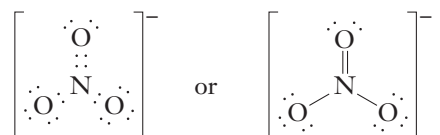
Check: 13 pairs of e^- have been used and all octets are satisfied. $2 \times 13 = 26e^-$ available.

For CH_3OH ,



Check: 7 pairs of e^- have been used and all octets are satisfied. $2 \times 7 = 14e^-$ available.

For NO_3^- ,



Check: 12 pairs of e^- have been used and all octets are satisfied. $2 \times 12 = 24e^-$ available.

EXAMPLE 7-1 Writing Lewis Formulas



Write the Lewis formula for the nitrogen molecule, N_2 .

Plan

We follow the stepwise procedure that was just presented for writing Lewis formulas.

Solution

Step 1: The skeleton is N N .

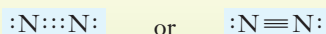
Step 2: $N = 2 \times 8 = 16e^-$ needed (total) by both atoms

$A = 2 \times 5 = 10e^-$ available (total) for both atoms

$S = N - A = 16e^- - 10e^- = 6e^-$ shared

Step 3: $\text{N}::\text{N}$ $6e^-$ (3 pairs) are shared; a *triple* bond.

Step 4: The additional $4e^-$ are accounted for by a lone pair on each N. The complete Lewis formula is



Check: $10e^-$ (5 pairs) have been used.

You should now work Exercise 30.

► We see that each N forms three bonds.

EXAMPLE 7-2 Writing Lewis Formulas



Write the Lewis formula for carbon disulfide, CS_2 , a foul-smelling liquid.

Plan

Again, we follow the stepwise procedure to apply the relationship $S = N - A$.

► C is the central atom, or the element in the middle of the molecule. It needs four more electrons to acquire an octet, and forms four bonds. Each S atom needs only two more electrons.

Solution

Step 1: The skeleton is S—C—S.

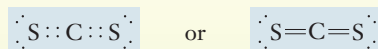
Step 2: $N = 1 \times 8$ (for C) + 2×8 (for S) = $24e^-$ needed by all atoms

$$A = 1 \times 4$$
 (for C) + 2×6 (for S) = $16e^-$ available

$$S = N - A = 24e^- - 16e^- = 8e^- \text{ shared}$$

Step 3: $S::C::S$ $8e^-$ (4 pairs) are shared; two *double* bonds.

Step 4: C already has an octet, so the remaining $8e^-$ are distributed as lone pairs on the S atoms to give each S an octet. The complete Lewis formula is



Check: $16e^-$ (8 pairs) have been used. The bonding picture is similar to that of CO_2 ; this is not surprising, because S is below O in Group 6A.

You should now work Exercise 32.

EXAMPLE 7-3 Writing Lewis Formulas

Write the Lewis formula for the carbonate ion, CO_3^{2-} .

Plan

The same stepwise procedure can be applied to ions. We must remember to adjust A , the total number of electrons, to account for the charge shown on the ion.

Solution

Step 1: The skeleton is $\begin{bmatrix} \text{O} \\ \text{O} \text{---} \text{C} \text{---} \text{O} \end{bmatrix}^{2-}$

Step 2: $N = 1 \times 8$ (for C) + 3×8 (for O) = $8 + 24 = 32e^-$ needed by all atoms

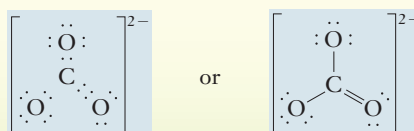
$$A = 1 \times 4$$
 (for C) + 3×6 (for O) + 2 (for the $2-$ charge)

$$= 4 + 18 + 2 = 24e^- \text{ available}$$

$$S = N - A = 32e^- - 24e^- = 8e^- \text{ (4 pairs) shared}$$

Step 3: $\begin{bmatrix} \text{O} \\ \text{O} \text{---} \text{C} \text{---} \text{O} \end{bmatrix}^{2-}$ (Four pairs are shared. At this point it doesn't matter which O is doubly bonded.)

Step 4: The Lewis formula is



Check: $24e^-$ (12 pairs) have been used.

You should now work Exercises 36 and 38.



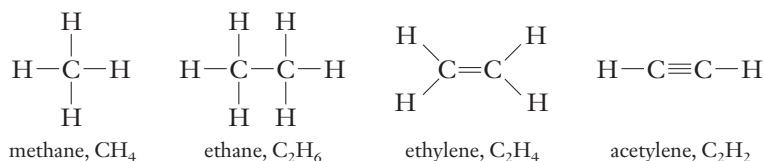
Charles D. Winters

Calcium carbonate, CaCO_3 , occurs in several forms in nature. The mineral calcite forms very large clear crystals (*right*); in microcrystalline form it is the main constituent of limestone (*top left*). Seashells (*bottom*) are largely calcium carbonate.

► We see that carbon forms four bonds.

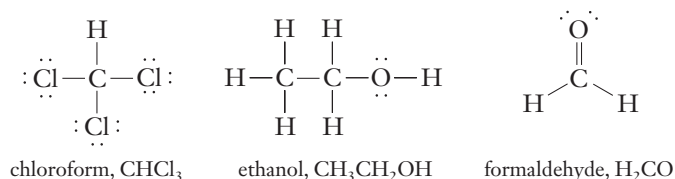
You should practice writing many Lewis formulas. A few common types of organic compounds and their Lewis formulas are shown here. Each follows the octet rule. Methane, CH_4 , is the simplest of a huge family of organic compounds called *hydrocarbons* (composed solely of hydrogen and carbon). Ethane, C_2H_6 , is another hydrocarbon that contains

only single bonds. Ethylene, C_2H_4 , has a carbon–carbon double bond, and acetylene, C_2H_2 , contains a carbon–carbon triple bond.



► For practice, apply the methods of this section to write these Lewis formulas. In each of these, carbon forms four bonds.

Halogen atoms can appear in place of hydrogen atoms in many organic compounds because hydrogen and halogen atoms each need one more electron to attain noble gas configurations. An example is chloroform, $CHCl_3$. Alcohols contain the group $C-O-H$; the most common alcohol is ethanol, CH_3CH_2OH . An organic compound that contains a carbon–oxygen double bond is formaldehyde, H_2CO .



Problem-Solving Tip Drawing Lewis Formulas

The following guidelines might help you draw Lewis formulas.

1. In most of their covalent compounds, the representative elements follow the octet rule, except that hydrogen always shares only two electrons.
2. Hydrogen forms only one bond to another element; thus hydrogen can never be a central atom.
3. Carbon forms four bonds (carbon monoxide, $:\text{C}\equiv\text{O}:$, and cyanide ion, $:\text{C}\equiv\text{N}:^-$, are prominent exceptions). This can be accomplished as:
 - a. four single bonds
 - b. two double bonds
 - c. two single bonds and one double bond or
 - d. one single bond and one triple bond
4. In neutral (uncharged) species, nitrogen forms three bonds, and oxygen forms two bonds.
5. In positive ions, nitrogen can form four bonds (e.g., NH_4^+) and oxygen can form three bonds (e.g., H_3O^+).
6. Nonmetals can form single, double, or triple bonds, but never quadruple bonds.
7. Carbon forms double or triple bonds to C, N, O, or S atoms; oxygen can form double bonds with many other elements.
8. Carbon is the only element that has a high tendency to form stable bonds with itself in compounds with other elements.

► C, N, and O often form double and triple bonds. S can form double bonds with C, N, and O.

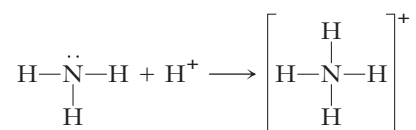
7-7 Formal Charges

Formal charge is the hypothetical charge on an atom *in a molecule or polyatomic ion*; to find the formal charge, we count bonding electrons as though they were equally shared between the two bonded atoms. The concept of formal charges helps us to write correct Lewis formulas in most cases. The most energetically favorable formula for a molecule is usually one in which the formal charge on each atom is zero or as near zero as possible.

Unless otherwise noted, all content on this page is © Cengage Learning.

► The H^+ ion has a vacant orbital, which accepts a share in the lone pair on nitrogen. The formation of a covalent bond by the sharing of an electron pair that is provided by one atom is called *coordinate covalent bond formation*. This type of bond formation is discussed again in Chapters 10 and 25.

Consider the reaction of NH_3 with hydrogen ion, H^+ , to form the ammonium ion, NH_4^+ .



The previously unshared pair of electrons on the N atom in the NH_3 molecule is shared with the H^+ ion to form the NH_4^+ ion, in which the N atom has four covalent bonds. Because N is a Group 5A element, we expect it to form three covalent bonds to complete its octet. How can we describe the fact that N has four covalent bonds in species like NH_4^+ ? The answer is obtained by calculating the *formal charge* on each atom in NH_4^+ by the following rules.

Rules for Assigning Formal Charges to Atoms of Group A Elements

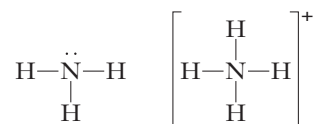
1. The formal charge, abbreviated FC, on an atom in a Lewis formula is given by the relationship

$$\text{FC} = (\text{group number}) - [(\text{number of bonds}) + (\text{number of unshared } e^-)]$$

Formal charges are represented by $\oplus$ and $\ominus$ to distinguish them from real charges on ions.

2. In a Lewis formula, an atom that has the same number of bonds plus unshared electrons as its periodic group number has a formal charge of zero.
3. a. In a molecule, the sum of the formal charges is zero.
b. In a polyatomic ion, the sum of the formal charges is equal to the charge on the ion.

Let us apply these rules to the ammonia molecule, NH_3 , and to the ammonium ion, NH_4^+ . Because N is a Group 5A element, its group number is 5.



In NH_3 the N atom has 3 bonds and 2 unshared e^- , and so for N,

$$\begin{aligned} \text{FC} &= (\text{group number}) - [(\text{number of bonds}) + (\text{number of unshared } e^-)] \\ &= 5 - (3 + 2) = 0 \quad (\text{for N}) \end{aligned}$$

For H,

$$\begin{aligned} \text{FC} &= (\text{group number}) - [(\text{number of bonds}) + (\text{number of unshared } e^-)] \\ &= 1 - (1 + 0) = 0 \quad (\text{for H}) \end{aligned}$$

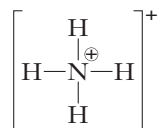
The formal charges of N and H are both zero in NH_3 , so the sum of the formal charges is $0 + 3(0) = 0$, consistent with Rule 3a.

In NH_4^+ the atom has four bonds and no unshared e^- , and so for N,

$$\begin{aligned} \text{FC} &= (\text{group number}) - [(\text{number of bonds}) + (\text{number of unshared } e^-)] \\ &= 5 - (4 + 0) = +1 \quad (\text{for N}) \end{aligned}$$

Calculation of the FC for H atoms gives zero, as shown previously. The sum of the formal charges in NH_4^+ is $(+1) + 4(0) = +1$. This is consistent with Rule 3b.

► FCs are indicated by $\oplus$ and $\ominus$.
The sum of the formal charges in a polyatomic ion is equal to the charge on the ion: $+1$ in NH_4^+ .



Unless otherwise noted, all content on this page is © Cengage Learning.

Thus, we see the octet rule is obeyed in both NH_3 and NH_4^+ . The sum of the formal charges in each case is that predicted by Rule 3, even though nitrogen has four covalent bonds in the NH_4^+ ion.

This bookkeeping system helps us to choose among various Lewis formulas for a molecule or ion, according to the following guidelines.

- The most likely formula for a molecule or ion is usually one in which the formal charge on each atom is zero or as near zero as possible.
- Negative formal charges are more likely to occur on the more electronegative elements.
- Lewis formulas in which adjacent atoms have formal charges of the same sign are usually *not* accurate representations (the *adjacent charge rule*).

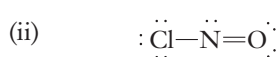
Now let's write some Lewis formulas for, and assign formal charges to, the atoms in nitrosyl chloride, NOCl , a compound often used in organic synthesis. The Cl atom and the O atom are both bonded to the N atom. Two Lewis formulas that satisfy the octet rule are



$$\text{For Cl, FC} = 7 - (2 + 4) = +1$$

$$\text{For N, FC} = 5 - (3 + 2) = 0$$

$$\text{For O, FC} = 6 - (1 + 6) = -1$$



$$\text{For Cl, FC} = 7 - (1 + 6) = 0$$

$$\text{For N, FC} = 5 - (3 + 2) = 0$$

$$\text{For O, FC} = 6 - (2 + 4) = 0$$

We believe that (ii) is a preferable Lewis formula because it has smaller formal charges than (i). We see that a double-bonded terminal Cl atom would have its electrons arranged as $\ddot{\text{Cl}}=\text{X}$, with the formal charge of Cl equal to $7 - (2 + 4) = +1$. A positive formal charge on such an electronegative element is quite unlikely, and double bonding to chlorine does not occur. The same reasoning would apply to the other halogens.

Problem-Solving Tip Calculating Formal Charges

A quick way to calculate formal charges for C, N, O, or F (and that generally holds for Cl, Br, and I as well) is to note the number of covalent bonds to that atom when it has an octet of electrons. The normal numbers of covalent bonds are: C = 4, N = 3, O = 2, and F = 1. For each bond that exceeds the normal number of covalent bonds, add a formal positive charge to that atom. For each atom that has fewer covalent bonds, add a formal negative charge for each missing covalent bond.

For example, consider carbon monoxide:



Each atom has an octet of electrons. The C atom, however, has only three covalent bonds, one fewer than usual, so it is assigned a formal charge of -1 . The O atom has three covalent bonds when it normally should have only two, so it is assigned a formal charge of $+1$.

In structure (i) of the previous example, $\ddot{\text{Cl}}=\ddot{\text{N}}-\ddot{\text{O}}:$, the Cl has two covalent bonds (normal = 4), so it is assigned a formal charge of $+1$. The O atom has only a single covalent bond (normal = 2), so it is assigned a formal charge of -1 . The N atom has three covalent bonds (normal = 3), so it has a formal charge of 0.

7-8 Writing Lewis Formulas: Limitations of the Octet Rule

Recall that representative elements achieve noble gas electron configurations in *most* of their compounds. But when the octet rule is not applicable, the relationship $S = N - A$ will not work without modification. The following are general cases for which the procedure in Section 7-6 *must be modified*—that is, there are four types of limitations of the octet rule.

Unless otherwise noted, all content on this page is © Cengage Learning.

► An atom cannot share in more than eight electrons using only *s* and *p* orbitals. To do so, it must have *d* or *f* valence shell orbitals. Thus, Limitation D can occur only for elements beyond Period 2.

► Lewis formulas are not normally written for compounds containing *d*- and *f*-transition metals. The *d*- and *f*-transition metals utilize *d* or *f* orbitals (or both) in bonding as well as *s* and *p* orbitals. Thus, they can accommodate more than eight valence electrons.

- A. Most covalent compounds of beryllium, Be. Because Be contains only two valence shell electrons, it usually forms only two covalent bonds when it bonds to two other atoms. We therefore use *four electrons* as the number *needed* by Be in Step 2. In Steps 3 and 4 we use only two pairs of electrons for Be.
 - B. Most covalent compounds of the Group 3A elements, especially boron, B. The 3A elements contain only three valence shell electrons, so they often form three covalent bonds when they bond to three other atoms. We therefore use *six electrons* as the number *needed* by the 3A elements in Step 2. In Steps 3 and 4 we use only three pairs of electrons for the 3A elements.
 - C. Compounds or ions containing an odd number of electrons. Examples are NO, with 11 valence shell electrons, and NO₂, with 17 valence shell electrons.
 - D. Compounds or ions in which the central element needs a share in more than eight valence shell electrons to hold all the available electrons, *A*. We say that the central atom in such species has an **expanded valence shell**. Extra rules are added to Steps 2 and 4 when this is encountered.
- Step 2a: If *S*, the number of electrons shared, is less than the number needed to bond all atoms to the central atom, then *S* is increased to the number of electrons needed.
- Step 4a: If *S* must be increased in Step 2a, then the octets of all the atoms might be satisfied before all of the electrons (*A*) have been added. Place the extra electrons on the central element.

Many species that violate the octet rule are quite reactive. For instance, compounds containing atoms with only four valence shell electrons (limitation type A) or six valence shell electrons (limitation type B) frequently react with other species that supply electron pairs. A compound that accepts a share in a pair of electrons is called a **Lewis acid**; a **Lewis base** is a species that makes available a share in a pair of electrons. (This kind of behavior will be discussed in detail in Section 10-10.) Molecules with an odd number of electrons often *dimerize* (combine in pairs) to give products that do satisfy the octet rule. Examples are the dimerization of NO to form N₂O₂ (Section 28-15) and NO₂ to form N₂O₄ (Section 28-15). Examples 7-4 through 7-8 illustrate some limitations and show how such Lewis formulas are constructed.

EXAMPLE 7-4 Limitation A of the Octet Rule



Write the Lewis formula for gaseous beryllium chloride, BeCl₂, a covalent compound.

Plan

This is an example of limitation type A. So, as we follow the steps in writing the Lewis formula, we must remember to use *four electrons* as the number *needed* by Be in Step 2. Steps 3 and 4 should show only two pairs of electrons for Be.

Solution

Step 1: The skeleton is Cl Be Cl

see limitation type A
↓

Step 2: $N = 2 \times 8$ (for Cl) + 1×4 (for Be) = $20e^-$ needed

$A = 2 \times 7$ (for Cl) + 1×2 (for Be) = $16e^-$ available

$S = N - A = 20e^- - 16e^- = 4e^-$ shared

Step 3: Cl: Be: Cl

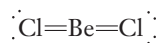
Step 4: $\text{:}\ddot{\text{Cl}}\text{: Be :}\ddot{\text{Cl}}\text{:}$ or $\text{:}\ddot{\text{Cl}}\text{---Be---}\ddot{\text{Cl}}\text{:}$

Calculation of formal charges shows that

for Be, $\text{FC} = 2 - (2 + 0) = 0$ and for Cl, $\text{FC} = 7 - (1 + 6) = 0$

In BeCl_2 , the chlorine atoms achieve the argon configuration, $[\text{Ar}]$, but the beryllium atom has a share of only four electrons. Compounds such as BeCl_2 , in which the central atom shares fewer than $8e^-$, are sometimes referred to as **electron-deficient compounds**. This “deficiency” refers only to satisfying the octet rule for the central atom. The term does not imply that there are fewer electrons than there are protons in the nuclei, as in the case of a cation, because the molecule is neutral.

A Lewis formula can be written for BeCl_2 that *does* satisfy the octet rule



Let us evaluate the formal charges for that formula:

$$\text{for Be, FC} = 2 - (4 + 0) = -2 \text{ and for Cl, FC} = 7 - (2 + 4) = +1$$

We have said that the most favorable structure for a molecule is one in which the formal charge on each atom is as near zero as possible. In case some atoms did have nonzero formal charges, we would expect that the more electronegative atoms (Cl) would be the ones with lowest formal charge. Thus, we prefer the Lewis structure shown in Example 7-4 over the double-bonded one above.

One might expect a similar situation for compounds of the other 2A metals, Mg, Ca, Sr, Ba, and Ra. These elements, however, have *lower ionization energies*, *lower electronegativities*, and *larger radii* than Be, so they usually form ions by losing two electrons. Mg, Ca, Sr, Ba, and Ra, therefore, form ionic compounds.

EXAMPLE 7-5 Limitation B of the Octet Rule



Write the Lewis formula for boron trichloride, BCl_3 , a covalent compound.

Plan

This covalent compound of boron is an example of limitation type B. As we follow the steps in writing the Lewis formula, we use *six electrons* as the number *needed* by boron in Step 2. Steps 3 and 4 should show only three pairs of electrons for boron.

Solution



Step 1: The skeleton is Cl — B — Cl

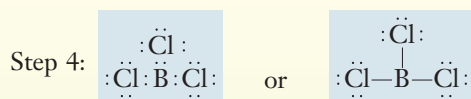
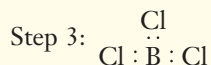
see limitation type B



Step 2: $N = 3 \times 8$ (for Cl) + 1×6 (for B) = $30e^-$ needed

$$A = 3 \times 7 \text{ (for Cl)} + 1 \times 3 \text{ (for B)} = 24e^- \text{ available}$$

$$S = N - A = 30e^- - 24e^- = 6e^- \text{ shared}$$



Each chlorine atom achieves the Ne configuration. The boron (central) atom acquires a share of only six valence shell electrons. Calculation of formal charges shows that

$$\text{for B, FC} = 3 - (3 + 0) = 0 \quad \text{and} \quad \text{for Cl, FC} = 7 - (1 + 6) = 0$$

You should now work Exercise 52.



Charles D. Winters

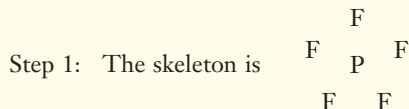
BF_3 and BCl_3 are gases at room temperature. Liquid BBr_3 and solid BI_3 are shown here.

EXAMPLE 7-6 Limitation D of the Octet Rule

Write the Lewis formula for phosphorus pentafluoride, PF_5 , a covalent compound.

Plan

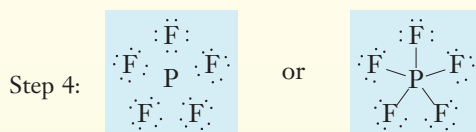
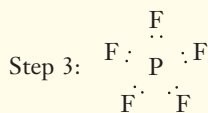
We apply the usual stepwise procedure to write the Lewis formula. In PF_5 , all five F atoms are bonded to P. This requires the sharing of a minimum of $10 e^-$, so this is an example of limitation type D. We therefore add Step 2a, and increase S from the calculated value of $8 e^-$ to $10 e^-$.

Solution

Step 2: $N = 5 \times 8$ (for F) + 1×8 (for P) = $48 e^-$ needed
 $A = 5 \times 7$ (for F) + 1×5 (for P) = $40 e^-$ available
 $S = N - A = 8 e^-$ shared

Five F atoms are bonded to P. This requires the sharing of a minimum of $10 e^-$. But only $8 e^-$ have been calculated. This is therefore an example of limitation type D.

Step 2a: Increase S from $8 e^-$ to $10 e^-$, the number required to bond five F atoms to one P atom. The number of electrons available, 40, does not change.



When the octets of the five F atoms have been satisfied, all 40 of the available electrons have been added. The phosphorus (central) atom has a share of 10 electrons.

Calculation of formal charges shows that

$$\text{for P, FC} = 5 - (5 + 0) = 0 \text{ and for F, FC} = 7 - (1 + 6) = 0$$

You should now work Exercise 56.

► An atom that exhibits an expanded valence shell is said to be **hypervalent**.

We see that P in PF_5 exhibits an expanded valence shell. The electronic basis of the octet rule is that one s and three p orbitals in the valence shell of an atom can accommodate a maximum of eight electrons. The valence shell of phosphorus has $n = 3$, so it also has $3d$ orbitals available that can be involved in bonding. The availability of valence shell d orbitals allows phosphorus (and many other representative elements of Period 3 and beyond) to exhibit an expanded valence shell. By contrast, elements in the *second row* of the periodic table can *never* exceed eight electrons in their valence shells because each atom has only one s and three p orbitals in that shell. Thus, we understand why PF_5 can exist but NF_5 cannot.

EXAMPLE 7-7 Limitation D of the Octet Rule

Write the Lewis formula for sulfur tetrafluoride, SF_4 .

Plan

We apply the usual stepwise procedure. The calculation of $S = N - A$ in Step 2 shows only $6e^-$ shared, but a minimum of $8e^-$ are required to bond four F atoms to the central S atom. Limitation type D applies, and we proceed accordingly.

Solution

Step 1: The skeleton is

$$\begin{array}{c} \text{F} \quad \text{S} \quad \text{F} \\ \text{F} \quad \text{F} \end{array}$$

Step 2: $N = 1 \times 8$ (S atom) + 4×8 (F atom) = $40e^-$ needed

$A = 1 \times 6$ (S atom) + 4×7 (F atom) = $34e^-$ available

$S = N - A = 40 - 34 = 6e^-$ shared. Four F atoms are bonded to the central S.

This requires a minimum of $8e^-$, but only $6e^-$ have been calculated in Step 2.

This is therefore an example of limitation type D.

Step 2a: We increase S from $6e^-$ to $8e^-$.

Step 3:

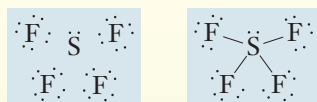
$$\begin{array}{c} \text{F} : \quad \text{S} : \quad \text{F} \\ : \quad : \quad : \\ \text{F} : \quad \text{F} \end{array}$$

Step 4:

$$\begin{array}{c} :\text{F}: \quad \text{S} : \quad :\text{F}: \\ :\text{F}: \quad :\text{F}: \end{array}$$

We first complete octets on the atoms around the central atom.

Step 4a: Now we have satisfied the octet rule, but we have used only 32 of the $34e^-$ available. We place the other two electrons on the central S atom.



Calculation of the formal charge shows that

$$\text{for S, FC} = 6 - (4 + 2) = 0$$

$$\text{for F, FC} = 7 - (1 + 6) = 0$$

You should now work Exercise 51.

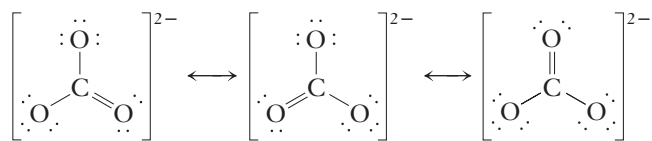
► The availability of valence shell d orbitals allows sulfur to have an expanded valence shell in SF_4 .

EXAMPLE 7-8 Limitation D of the Octet Rule

Write the Lewis formula for the triiodide ion, I_3^- .

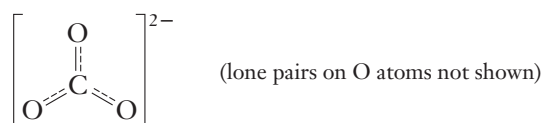
Plan

We apply the usual stepwise procedure. The calculation of $S = N - A$ in Step 2 shows only $2e^-$ shared, but at least $4e^-$ are required to bond two I atoms to the central I. Limitation type D applies, and we proceed accordingly.



A molecule or polyatomic ion for which two or more Lewis formulas *with the same arrangements of atoms* can be drawn to describe the bonding is said to exhibit **resonance**. The three structures shown here are *resonance structures* of the carbonate ion. The relationship among them is indicated by the double-headed arrows, $\leftrightarrow$. This symbol *does not mean* that the ion flips back and forth among these three structures. The true structure can be described as an average, or hybrid, of the three.

Experiments show that the C—O bonds in CO_3^{2-} are *neither* double nor single bonds but are intermediate in bond length and strength. Based on measurements in many compounds, the typical C—O single bond length is 1.43 Å, and the typical C=O double bond length is 1.22 Å. The C—O bond length for each bond in the CO_3^{2-} ion is intermediate at 1.29 Å. Another way to represent this situation is by **delocalization** of bonding electrons:



The dashed lines indicate that some of the electrons shared between C and O atoms are *delocalized* among all four atoms; that is, the four pairs of shared electrons are equally distributed among three C—O bonds.

► When electrons are shared among more than two atoms, the electrons are said to be *delocalized*. The concept of delocalization is important in molecular orbital theory (see Chapter 9).

EXAMPLE 7-9 Lewis Formulas, Resonance



Draw two resonance structures for the sulfur dioxide molecule, SO_2 .

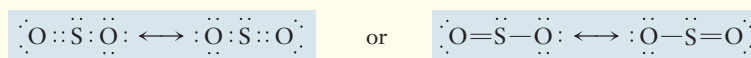
Plan

The stepwise procedure (see Section 7-6) can be used to write each resonance structure.

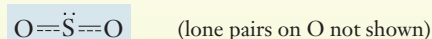
Solution

$$\begin{array}{rcl}
 \begin{array}{cc} \text{S} & \text{O} \\ \searrow & \searrow \end{array} & & \\
 N = 1(8) + 2(8) = 24e^- & & \\
 A = 1(6) + 2(6) = 18e^- & & \\
 \hline
 S = N - A & = & 6e^- \text{ shared}
 \end{array}$$

The resonance structures are



We could show delocalization of electrons as follows:



Remember that Lewis formulas *do not necessarily show shapes*. SO_2 molecules are angular, not linear.

You should now work Exercises 60 and 62.



Charles D. Winters

The rose on the left is in an atmosphere of sulfur dioxide, SO_2 . Gaseous SO_2 and its aqueous solutions are used as bleaching agents. A similar process is used to bleach wood pulp before it is converted to paper.

Problem-Solving Tip Some Guidelines for Resonance Structures

Resonance involves several different acceptable Lewis formulas with the same arrangement of atoms. Resonance structures cannot differ in atom positions, only in the arrangements of electron pairs. The actual structure of such a molecule or ion is the average, or composite, of its resonance structures, but this does not mean that the electronic structure is jumping between these arrangements. This average structure is more stable than any of the individual resonance structures.

7-10 Polar and Nonpolar Covalent Bonds

Covalent bonds may be either *polar* or *nonpolar*. In a **nonpolar bond** such as that in the hydrogen molecule, H_2 ($H:H$ or $H-H$), the electron pair is *shared equally* between the two hydrogen nuclei. We defined electronegativity as the tendency of an atom to attract electrons to itself in a chemical bond (see Section 5-6). Both H atoms have the same electronegativity. This means that the shared electrons are equally attracted to both hydrogen nuclei and therefore spend equal amounts of time near each nucleus. In this nonpolar covalent bond, the *electron density* is symmetrical about a plane that is perpendicular to a line between the two nuclei. This is true for all homonuclear *diatomic molecules*, such as H_2 , O_2 , N_2 , F_2 , and Cl_2 , because the two identical atoms have identical electronegativities. We can generalize:

The covalent bonds in all homonuclear diatomic molecules must be nonpolar.

Let us now consider *heteronuclear diatomic molecules*. Start with the fact that hydrogen fluoride, HF, is a gas at room temperature. This tells us that it is a covalent compound because ionic compounds are solids at room temperature. We also know that the $H-F$ bond has some degree of polarity because H and F are not identical atoms and therefore do not attract the electrons equally. But how polar will this bond be?

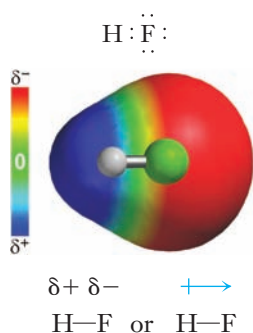
The electronegativity of hydrogen is 2.1, and that of fluorine is 4.0 (see Table 5-3). The F atom, with its higher electronegativity, attracts the shared electron pair much more strongly than does the H atom. We can represent the structure of HF as shown in the margin. The electron density is distorted in the direction of the more electronegative fluorine atom, making F more negative. This small shift of electron density leaves H somewhat positive.

Covalent bonds, such as the one in HF, in which the *electron pairs are shared unequally* are called **polar covalent bonds**. Two kinds of notation used to indicate polar bonds are shown in the margin.

The $\delta-$ over the F atom indicates a “partial negative charge.” This means that the F end of the molecule is somewhat more negative than the H end. The $\delta+$ over the H atom indicates a “partial positive charge,” or that the H end of the molecule is positive *with respect to* the F end. We are *not* saying that H has a charge of $1+$ or that F has a charge of $1-$! A second way to indicate the polarity is to draw an arrow so that the head points toward the negative end (F) of the bond and the crossed tail, which resembles a positive sign, indicates the positive end (H).

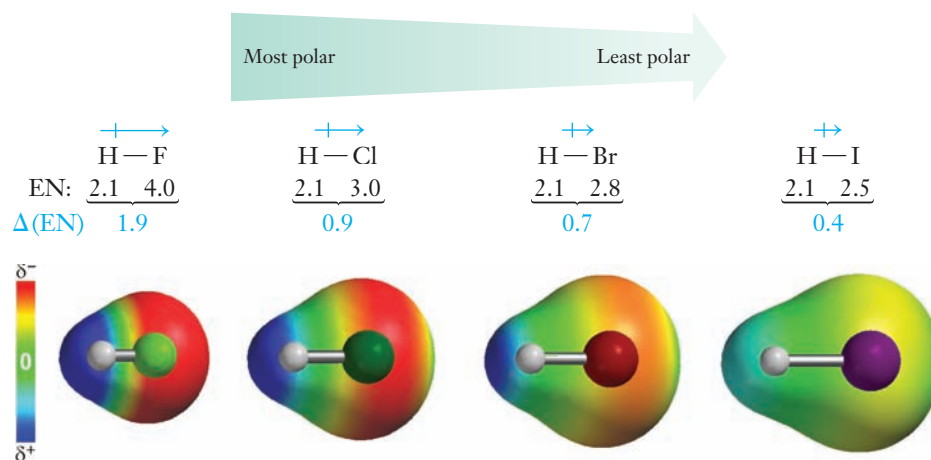
The separation of charge in a polar covalent bond creates an electric **dipole**. We expect the dipoles in the covalent molecules HF, HCl, HBr, and HI to be different because F, Cl, Br, and I have different electronegativities. This tells us that atoms of these elements have different tendencies to attract an electron pair that they share with hydrogen. We indicate this difference as shown here, where $\Delta(EN)$ is the difference in electronegativity between two atoms that are bonded together.

► A **homonuclear** molecule contains only one kind of atom. A molecule that contains two or more kinds of atoms is described as **heteronuclear**.



► The word “dipole” means “two poles.” Here it refers to the positive and negative poles that result from the separation of charge within a molecule. In physics the dipole arrow has the opposite definition, with the crossed tail indicating the negative charge and the arrow head the positive charge. We will use the standard chemistry notation where the arrow points from the positive charge toward the negative charge.

Unless otherwise noted, all content on this page is © Cengage Learning.



► The values of electronegativity are obtained from Table 5-3.

The longest arrow indicates the largest dipole, or greatest separation of electron density in the molecule (Table 7-5). For comparison, the $\Delta(\text{EN})$ values for some typical 1:1 ionic compounds are RbCl, 2.1; NaF, 3.0; and KCl, 2.1.

EXAMPLE 7-10 Polar Bonds



Each halogen can form single covalent bonds with other halogens, to form compounds called *interhalogens*; some examples are ClF and BrF. Use the electronegativity values in Table 5-3 to rank the following single bonds from most polar to least polar: F—F, F—Cl, F—Br, Cl—Br, Cl—I, and Cl—Cl.

Plan

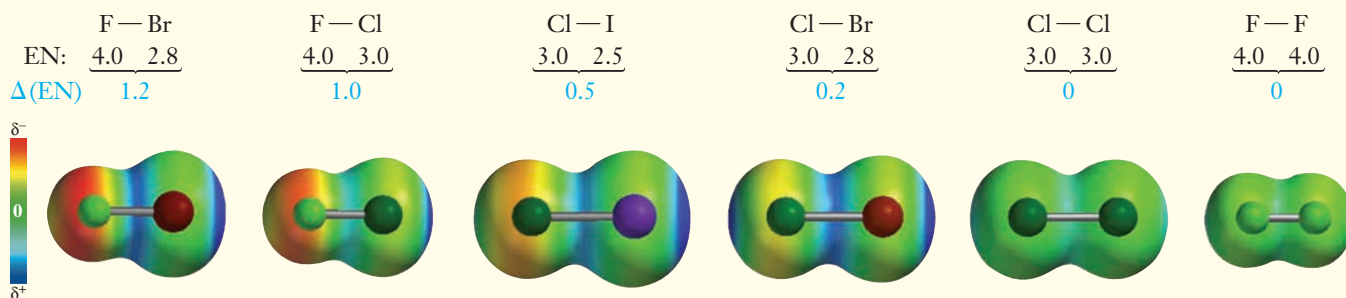
The bond polarity decreases as the electronegativity difference between the two atoms decreases. We can calculate $\Delta(\text{EN})$ for each bond and then arrange them according to decreasing $\Delta(\text{EN})$ value.

Solution

We know that two F atoms have the same electronegativity, so $\Delta(\text{EN})$ for F—F must be zero, and the F—F bond is nonpolar; the same reasoning applies to Cl—Cl. We use the values from Table 5-3 to calculate $\Delta(\text{EN})$ for each of the other pairs, always subtracting the smaller from the larger value:

Elements	$\Delta(\text{EN})$
F, Cl	$4.0 - 3.0 = 1.0$
F, Br	$4.0 - 2.8 = 1.2$
Cl, Br	$3.0 - 2.8 = 0.2$
Cl, I	$3.0 - 2.5 = 0.5$

The bonds, arranged from most polar to least polar, are



We know that the halogens, like the elements in any column in the periodic table, decrease in electronegativity going down the group. In this example, F and Br are the two halogens with the greatest separation in the column, so they have the biggest electronegativity difference. Thus the F—Br bond is the most polar bond in this example, more polar than F—Cl. Two like atoms have equal attraction for the shared electrons, so any X—X bond such as Cl—Cl or F—F must be nonpolar. (Your instructor may require you to predict some relative bond polarities from reasoning such as this, even without numerical values of electronegativity.)

You should now work Exercise 74.

7-11 Dipole Moments

It is convenient to express bond polarities on a numerical scale. We indicate the polarity of a molecule by its dipole moment, which measures the separation of charge within the molecule. The **dipole moment**, μ , is defined as the product of the distance, d , separating charges of equal magnitude and opposite sign, and the magnitude of the charge, q . A dipole moment is measured by placing a sample of the substance between two plates and applying a voltage. This causes a small shift in electron density of any molecule, so the applied voltage is diminished very slightly. Diatomic molecules that contain polar bonds, however, such as HF, HCl, and CO, tend to orient themselves in the electric field (Figure 7-5). This causes the measured voltage between the plates to decrease more markedly for these substances, and we say that these molecules are *polar*. Molecules such as F₂ or N₂ do not reorient, so the change in voltage between the plates remains slight; we say that these molecules are *nonpolar*.

Generally, as electronegativity differences increase in diatomic molecules, the measured dipole moments increase. This can be seen clearly from the data for the hydrogen halides (see Table 7-5).

Unfortunately, the dipole moments associated with *individual bonds* can be measured only in simple diatomic molecules. *Entire molecules* rather than selected pairs of atoms must be used for experimental measurement. Measured values of dipole moments thus reflect the *overall* polarities of molecules. For polyatomic molecules they are the result of all the bond dipoles in the molecules. In Chapter 8, we will see that structural features, such as molecular geometry and the presence of lone (unshared) pairs of electrons, also affect the polarity of a molecule.

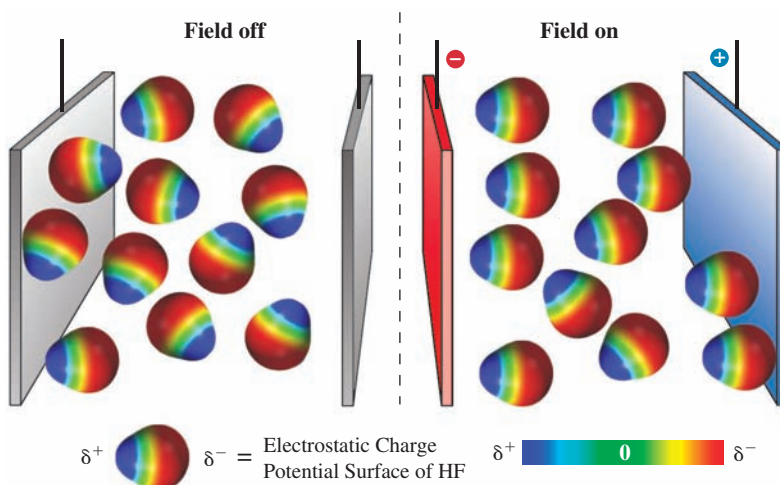
► $\mu = d \times q$

Table 7-5 $\Delta(\text{EN})$ Values and Dipole Moments for Some Pure (Gaseous) Substances

Substance	$\Delta(\text{EN})$	Dipole Moment (μ)*
HF	1.9	1.91 D
HCl	0.9	1.03 D
HBr	0.7	0.79 D
HI	0.4	0.38 D
H ₂	0.0	0.00 D

*Molecular dipole moments are usually expressed in debyes (D).

Figure 7-5 If polar molecules, such as HF, are subjected to an electric field, they tend to line up very slightly in a direction opposite to that of the field. This minimizes the electrostatic energy of the molecules. Nonpolar molecules are not oriented by an electric field. The effect is greatly exaggerated in this drawing.



Unless otherwise noted, all content on this page is © Cengage Learning.

7-12 The Continuous Range of Bonding Types

Now let's clarify our classification of bonding types. The degree of electron sharing or transfer depends on the electronegativity difference between the bonding atoms. Nonpolar covalent bonding (involving *equal sharing* of electron pairs) is one extreme, occurring when the atoms are identical ($\Delta[\text{EN}]$ is zero). Ionic bonding (involving *complete transfer* of electrons) represents the other extreme, and occurs when two elements with very different electronegativities interact ($\Delta[\text{EN}]$ is large).

Polar covalent bonds may be thought of as intermediate between pure (nonpolar) covalent bonds and pure ionic bonds. In fact, bond polarity is sometimes described in terms of *partial ionic character*. This usually increases with increasing difference in electronegativity between bonded atoms. Calculations based on the measured dipole moment of gaseous HCl indicate about 17% “ionic character.”

When cations and anions interact strongly, some amount of electron sharing takes place; in such cases we can consider the ionic compound as having some *partial covalent character*. For instance, the high charge density of the very small Li^+ ion causes it to distort large anions that it approaches. The distortion attracts electron density from the anion to the region between it and the Li^+ ion, giving lithium compounds a higher degree of covalent character than in other alkali metal compounds.

Almost all bonds have both ionic and covalent character. By experimental means, a given type of bond usually can be identified as being “closer” to one or the other extreme type. We find it useful and convenient to use the labels for the major classes of bonds to describe simple substances, keeping in mind that they represent ranges of behavior.

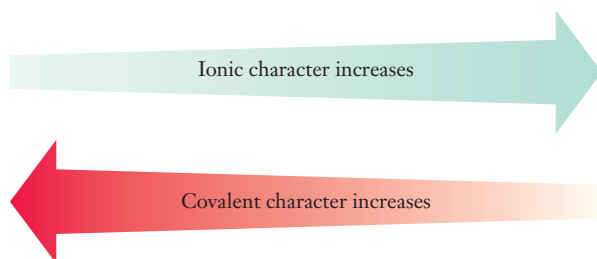
Above all, we must recognize that any classification of a compound that we might suggest based on electronic properties *must* be consistent with the physical properties of ionic and covalent substances described at the beginning of the chapter. For instance, HCl has a rather large electronegativity difference (0.9), and its aqueous solutions conduct electricity. But we know that we cannot view it as an ionic compound because it is a gas, and not a solid, at room temperature. Liquid HCl is a nonconductor.

► HCl *ionizes* in aqueous solution. We will study more about this behavior in Chapter 10.

Let us point out another aspect of the classification of compounds as ionic or covalent. Not all ions consist of single charged atoms. Many are small groups of atoms that are covalently bonded together, yet they still have excess positive or negative charge. Examples of such *polyatomic ions* are ammonium ion, NH_4^+ , sulfate ion, SO_4^{2-} , and nitrate ion, NO_3^- . A compound such as potassium sulfate, K_2SO_4 , contains potassium ions, K^+ , and sulfate ions, SO_4^{2-} , in a 2:1 ratio. We should recognize that this compound contains both covalent bonding (electron sharing *within* each sulfate ion) and ionic bonding (electrostatic attractions *between* potassium and sulfate ions). We classify this compound as *ionic*, however, because it is a high-melting solid (mp = 1069°C), it conducts electricity both in molten form and in aqueous solution, and it displays other properties that we generally associate with ionic compounds. Put another way, covalent bonding holds each sulfate ion together, but the forces that hold the *entire* substance together are ionic, so the compound is classified as ionic.

In summary, we can describe chemical bonding as a continuum that may be represented as

$\Delta(\text{EN})$ for the bonding atoms	zero	→	intermediate	→	large
Bonding types	nonpolar covalent	→	polar covalent	→	ionic



KEY TERMS

Anion A negatively charged ion; that is, an ion in which the atom or group of atoms has more electrons than protons.

Binary compound A compound consisting of two elements; may be ionic or covalent.

Bond dissociation energy The stabilization of a bonded pair of atoms compared to the same atoms when separated; the energy required to break the bonding between a pair of atoms; also known as *bond energy*.

Bond energy See *Bond dissociation energy*.

Bonding pair A pair of electrons involved in a covalent bond; also known as *shared pair*.

Bond length The distance between the centers (nuclei) of two bonded atoms.

Cation A positively charged ion; that is, an ion in which the atom or group of atoms has fewer electrons than protons.

Chemical bonds Attractive forces that hold atoms together in elements and compounds.

Covalent bond A chemical bond formed by the sharing of one or more electron pairs between two atoms.

Covalent compound A compound containing predominantly covalent bonds.

Debye The unit used to express dipole moments.

Delocalization of electrons Refers to bonding electrons distributed among more than two atoms that are bonded together; occurs in species that exhibit resonance.

Dipole Refers to the separation of charge between two covalently bonded atoms.

Dipole moment (μ) The product of the distance separating opposite charges of equal magnitude and the magnitude of the charge; a measure of the polarity of a bond or molecule. A measured dipole moment refers to the dipole moment of an entire molecule.

Double bond A covalent bond resulting from the sharing of four electrons (two pairs) between two atoms.

Electron-deficient compound A compound containing at least one atom (other than H) that has fewer than eight valence shell electrons.

Expanded valence shell Describes a Group A (representative) atom that contains more than eight valence shell electrons.

Formal charge The hypothetical charge on an atom in a covalently bonded molecule or ion; bonding electrons are counted as though they were shared equally between the two bonded atoms.

Heteronuclear Consisting of different elements.

Homonuclear Consisting of only one element.

Hypervalent See *Expanded valence shell*.

Ion An atom or a group of atoms that carries an electrical charge.

Ionic bonding The attraction of oppositely charged ions (cations and anions) in large numbers to form a solid. Ions result from the transfer of one or more electrons from one atom or group of atoms to another.

Ionic compound A compound containing predominantly ionic bonding.

Lewis acid A substance that accepts a share in a pair of electrons from another species.

Lewis base A substance that makes available a share in an electron pair.

Lewis formula The representation of a molecule, ion, or formula unit by showing atomic symbols and only outer-shell electrons; does not represent the shape of the molecule or ion. Each bonding electron pair can be represented by a pair of dots (the Lewis dot formula) or by a dash (the Lewis dash formula).

Lone pair A pair of electrons residing on one atom and not shared by other atoms; also known as *unshared pair*.

Monatomic ion An ion that consists of only one atom.

Nonpolar bond A covalent bond between two atoms with the same electronegativity so that the electron density is symmetrically distributed.

Octet rule Many representative elements attain at least a share of eight electrons in their valence shells when they form molecular or ionic compounds; this rule has some limitations.

Polar bond A covalent bond between two atoms with different electronegativities so that the electron density is unsymmetrically distributed.

Polyatomic ion An ion that consists of more than one atom.

Resonance A concept in which two or more Lewis formulas for the same arrangement of atoms (resonance structures) are used to describe the bonding in a molecule or ion.

Single bond A covalent bond resulting from the sharing of two electrons (one pair) between two atoms.

Triple bond A covalent bond resulting from the sharing of six electrons (three pairs) between two atoms.

Unshared pair See *Lone pair*.

Valence electrons The electrons in the outermost shell of an atom.

EXERCISES

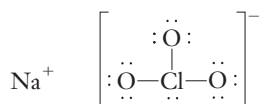
● Molecular Reasoning exercises

▲ More Challenging exercises

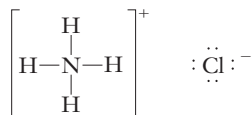
Blue-Numbered exercises are solved in the Student Solutions Manual

Chemical Bonding: Basic Ideas

1. ● What type of force is responsible for chemical bonding? Explain the differences between ionic bonding and covalent bonding.
2. ● What kind of bonding (ionic or covalent) would you predict for the products resulting from the following combination of elements? (a) $K + Cl_2$; (b) $C + O_2$; (c) $N_2 + O_2$; (d) $S + O_2$.
3. Why are covalent bonds called directional bonds, whereas ionic bonding is termed nondirectional?
4. (a) What do Lewis dot formulas for atoms show? (b) Write Lewis dot formulas for the following atoms: He, Si, P, Ne, Mg, I.
5. Write Lewis dot formulas for the following atoms: B, C, S, Ar, Ge, Te.
6. ● Describe the types of bonding in sodium chlorate, $NaClO_3$.



7. ● Describe the types of bonding in ammonium chloride, NH_4Cl .



8. ● Based on the positions in the periodic table of the following pairs of elements, predict whether bonding between the two would be primarily ionic or covalent. Justify your answers. (a) Ca and Cl; (b) P and O; (c) Br and I; (d) Na and I; (e) Si and Br; (f) Ba and F.
9. ● Predict whether the bonding between the following pairs of elements would be primarily ionic or covalent. Justify your answers. (a) Rb and Cl; (b) N and O; (c) Ca and F; (d) N and S; (e) C and F; (f) K and O.
10. ● Classify the following compounds as ionic or covalent: (a) $Ca(NO_3)_2$; (b) H_2Se ; (c) KNO_3 ; (d) $CaCl_2$; (e) H_2CO_3 ; (f) NCl_3 ; (g) Li_2O ; (h) N_2H_4 ; (i) $SOCl_2$.

Ionic Bonding

11. Describe what happens to the valence electron(s) as a metal atom and a nonmetal atom combine to form an ionic compound.

12. ▲ Describe an ionic crystal. What factors might determine the geometrical arrangement of the ions?
13. ● Why are solid ionic compounds rather poor conductors of electricity? Why does conductivity increase when an ionic compound is melted or dissolved in water?
14. Write the formula for the ionic compound that forms between each of the following pairs of elements: (a) Li and O_2 ; (b) K and Se; (c) Mg and Br_2 .
15. Write the formula for the ionic compound that forms between each of the following pairs of elements: (a) Li and O_2 ; (b) K and Se; (c) Mg and Br_2 .
16. When a *d*-transition metal ionizes, it loses its outer *s* electrons before it loses any *d* electrons. Using [noble gas] (*n* - 1) *d^x* representations, write the outer-electron configurations for the following ions: (a) Cr^{3+} ; (b) Mn^{2+} ; (c) Ag^+ ; (d) Fe^{3+} ; (e) Cu^{2+} ; (f) Sc^{2+} ; (g) Fe^{2+} .
17. ● Which of the following do not accurately represent stable binary ionic compounds? Why? $MgBr_3$, NaS , AlF_4 , SrS_2 , Ca_2O_3 , $NaBr_2$, NCl_4 , $LiSe_2$, NaO .
18. ● Which of the following do not accurately represent stable binary ionic compounds? Why? MgI , $Al(OH)_2$, InF_2 , CO_4 , $RbCl_2$, CsS , Be_3O .
19. ● (a) Write Lewis formulas for the positive and negative ions in these compounds: $SrBr_2$, K_2O , Ca_3P_2 , GaF_3 , Bi_2O_3 . (b) Which ions do not have a noble gas configuration?
20. Write formulas for two cations that have the following valence shell electron configuration: (a) $3s^23p^6$; (b) $6s^26p^6$.
21. Write formulas for two anions that have each of the electron configurations listed in Exercise 20.

Covalent Bonding: General Concepts

22. ● What does Figure 7-4 tell us about the attractive and repulsive forces in a hydrogen molecule?
23. ● Distinguish between heteronuclear and homonuclear diatomic molecules.
24. How many electrons are shared between two atoms in (a) a single covalent bond, (b) a double covalent bond, and (c) a triple covalent bond?
25. What is the maximum number of covalent bonds that a second-period element could form? How can the representative elements beyond the second period form more than this number of covalent bonds?
26. ● Complete the following chart using data found in Tables 7-3 and 7-4. Compare the energies and lengths of single, double, and triple bonds of carbon to oxygen. Then compare the changes between single-, double-, and triple-

● Molecular Reasoning exercises

▲ More Challenging exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

bonded carbon to oxygen to the similar changes in carbon bonded to carbon.

	Single Bond C—O	Double Bond C=O	Triple Bond C≡O
Bond energy (kJ/mol)	—	—	—
Bond length (Å)	—	—	—

27. Complete the following chart using data found in Tables 7-3 and 7-4. Compare the energies and lengths of single, double, and triple bonds of carbon to nitrogen. Then compare the changes between single-, double-, and triple-bonded carbon to nitrogen to the similar changes in carbon bonded to carbon.

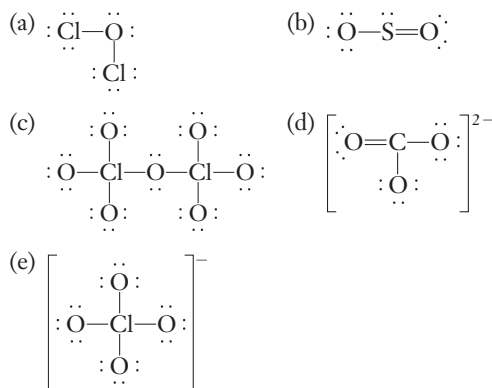
	Single Bond C—N	Double Bond C=N	Triple Bond C≡N
Bond energy (kJ/mol)	—	—	—
Bond length (Å)	—	—	—

Lewis Formulas for Molecules and Polyatomic Ions

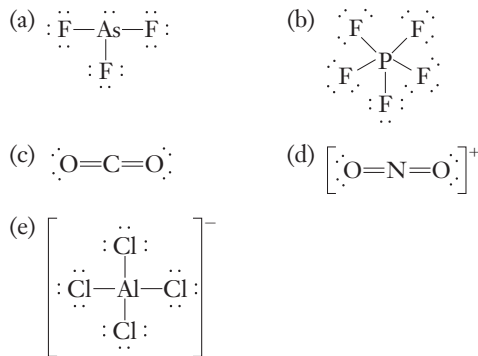
28. What information about chemical bonding can a Lewis formula give for a compound or ion? What information about bonding is not directly represented by a Lewis formula?
29. Write Lewis formulas for the following: H_2 , N_2 , I_2 , HCl , HI .
30. Write Lewis formulas for the following: H_2O , NH_3 , OH^- , Br^- .
31. Use Lewis formulas to represent the covalent molecules formed by these pairs of elements. Write only structures that satisfy the octet rule. (a) P and H; (b) As and Br; (c) N and Cl; (d) Si and Cl.
32. Use Lewis formulas to represent the covalent molecules formed by these pairs of elements. Write only structures that satisfy the octet rule. (a) S and Cl; (b) As and F; (c) I and Cl; (d) Se and Cl.
33. Find the total number of valence electrons in each of the following molecules or ions: (a) NH_2^- ; (b) ClO_2^- ; (c) HCN ; (d) SnCl_4 .
34. How many valence electrons does each of these molecules or ions have? (a) H_2Se ; (b) PCl_3 ; (c) ClO_4^- ; (d) OH^- .
35. Write Lewis structures for the molecules or ions in Exercise 33.
36. Write Lewis structures for the molecules or ions in Exercise 34.
37. Write Lewis structures for the following molecules or ions: (a) ClO_3^- ; (b) $\text{C}_2\text{H}_6\text{O}$ (two possibilities); (c) HOCl ; (d) SO_3^{2-} .
38. Write Lewis structures for the following molecules or ions: (a) H_2CO ; (b) ClBr ; (c) BF_4^- ; (d) PO_4^{3-} ; (e) HClO_3 .
39. Name an element with which nitrogen would form: (a) a mostly ionic bond, (b) a polar covalent bond, and (c) a nonpolar covalent bond (other than another nitrogen atom). How did you determine which elements would form each type of bond with nitrogen? Does the element that forms a polar covalent bond with nitrogen form a polar covalent bond with every element?
40. Why do atoms of two nonmetals generally form a compound by sharing valence electrons, rather than by transferring electrons, as in the formation of ionic compounds?
41. Write Lewis structures for these molecules or ions. (a) ClF ; (b) H_2Se ; (c) BF_4^- ; (d) PO_4^{3-} .
42. Write Lewis formulas for CCl_4 , SiF_4 , and PbI_4 . Explain the similarity.

Formal Charges

43. Assign a formal charge to each atom in the following:



44. Assign a formal charge to each atom in the following:

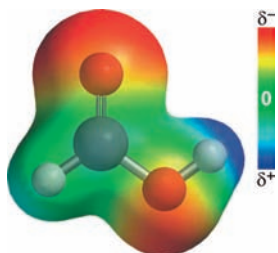


45. What is the formal charge on the indicated atom in each of the following species? (a) sulfur in SO_2 ; (b) nitrogen in N_2H_4 ; (c) each oxygen atom in ozone, O_3 .
46. Write Lewis formulas for six different resonance forms of the sulfate ion, SO_4^{2-} . Indicate all formal charges. Predict which arrangement is likely to be the least stable and justify your selection. (*Hint:* The answer must include resonance structures that have more than an octet of electrons about the sulfur atom.)
47. The formula of the thiocyanate ion is SCN^- . Draw two Lewis formulas for this ion, one with two double bonds and one with a single bond and a triple bond.

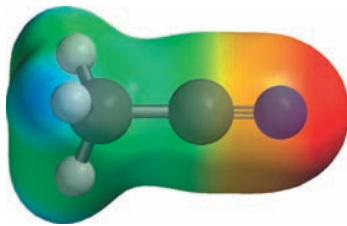
Calculate the formal charges on each atom in each Lewis formula. Which structure is more likely?

More Lewis Formulas

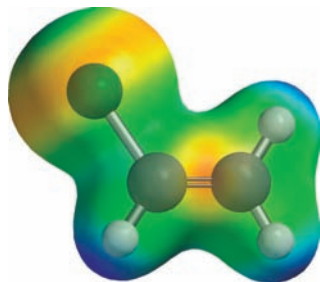
48. Write Lewis formulas for butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, and propane, $\text{CH}_3\text{CH}_2\text{CH}_3$. Describe the nature of the bond indicated: $\text{CH}_3\text{CH}_2-\text{CH}_2\text{CH}_3$ and $\text{CH}_3-\text{CH}_2\text{CH}_3$.
49. Write Lewis structures for the following molecules:
- (a) formic acid, HCOOH , in which the ECP plot is:



- (b) acetonitrile, CH_3CN ;



- (c) vinyl chloride, CH_2CHCl , the molecule from which PVC plastics are made.



Charles D. Winters

PVC Pipe

50. Write Lewis structures for the following molecules: (a) tetrafluoroethylene, C_2F_4 , the molecule from which Teflon is made; (b) acrylonitrile, CH_2CHCN , the molecule from which Orlon is made.



Charles D. Winters

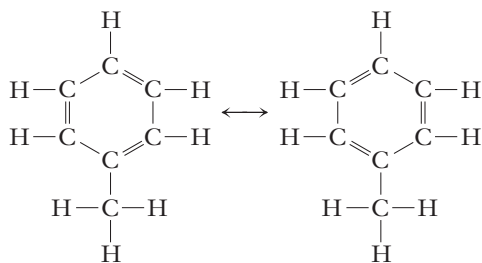
Teflon-coated pan

Limitation of the Octet Rule

51. Draw Lewis formulas for sulfur difluoride (SF_2) and sulfur hexafluoride (SF_6). Is either one an exception to the octet rule?
52. Write the Lewis formula for each of the following covalent compounds. Which ones contain at least one atom with a share in less than an octet of valence electrons? (a) BeBr_2 ; (b) BBr_3 ; (c) NCl_3 ; (d) AlCl_3 .
53. Which of the following species contain at least one atom that is an exception to the octet rule?
- (a) $\text{F}-\text{Cl}$ (b) $\text{O}-\text{Cl}-\text{O}$ (c) $\text{F}-\text{Xe}-\text{F}$
- (d) $\left[\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \text{:}\ddot{\text{O}}-\text{Cl}-\ddot{\text{O}}\text{:} \\ \text{:}\ddot{\text{O}}\text{:} \end{array} \right]^-$
54. Write the Lewis formula for each of the following molecules or ions. Which ones contain at least one atom with a share in less than an octet of valence electrons? (a) CH_2Cl_2 ; (b) BF_3 ; (c) BCl_4^- ; (d) AlF_4^- .
55. None of the following is known to exist. What is wrong with each one?
- (a) $\text{Cl}-\text{S}=\text{O}$ (d) $\text{Na}-\ddot{\text{O}}\text{:}$
Na
- (b) $\text{H}-\text{H}-\ddot{\text{O}}-\ddot{\text{P}}-\ddot{\text{Cl}}\text{:}$ (e) $\text{:}\ddot{\text{O}}\text{:}\ddot{\text{O}}\text{:}\ddot{\text{Cl}}\text{:}$
Cl
- (c) $\text{O}\equiv\text{N}-\ddot{\text{O}}\text{:}$
56. In which of the following does the central atom obey the octet rule: NO_2 , SF_4 , NH_3 , SO_3 , ClO_2 , and ClO_2^- ? Are any of these species odd-electron molecules or ions?

Resonance Structures

57. What do we mean by the term “resonance”? Do the resonance structures that we draw actually represent the bonding in the substance? Explain your answer.
58. ● Careful examination of the ozone molecule indicates that the two outer oxygens are the same distance from the central oxygen. Write Lewis formulas or resonance structures that are consistent with this finding.
59. Draw resonance structures for (a) NO_2^- ; (b) NNO ; (c) HCO_2^- .
60. ▲ We can write two resonance structures for toluene, $\text{C}_6\text{H}_5\text{CH}_3$:

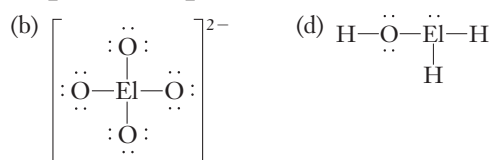
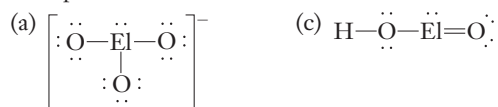


How would you expect the carbon–carbon bond lengths in the six-membered ring of toluene to compare with the carbon–carbon bond length between the CH_3 group and the carbon atom on the ring?

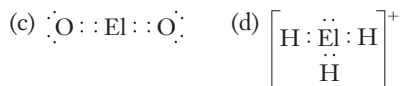
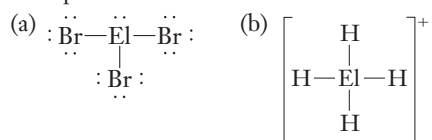
61. Write resonance structures for the acetate ion, CH_3COO^- .
62. ● Write resonance structures for each of the following ions. (a) NO_2^- ; (b) BrO_3^- ; (c) PO_4^{3-} . (*Hint*: Consider both the Br and the P to share more than an octet of electrons in order for them to also form at least one double bond.)

Mixed Exercises

63. ●▲ Suppose that “El” is the general symbol for a representative element. In each case, in which periodic group is El located? Justify your answers and cite a specific example for each one.



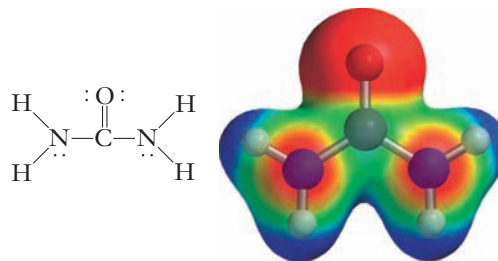
64. ●▲ Suppose that “El” is the general symbol for a representative element. In each case, in which periodic group is El located? Justify your answers and cite a specific example for each one.



65. ● Many common stains, such as those of chocolate and other fatty foods, can be removed by dry-cleaning solvents such as tetrachloroethylene, C_2Cl_4 . Is C_2Cl_4 ionic or covalent? Write its Lewis formula.
66. ●▲ Write acceptable Lewis formulas for the following common air pollutants: (a) SO_2 ; (b) NO_2 ; (c) CO ; (d) O_3 (ozone); (e) SO_3 ; (f) $(\text{NH}_4)_2\text{SO}_4$. Which one is a solid? Which ones exhibit resonance? Which ones violate the octet rule?

Ionic Versus Covalent Character and Bond Polarities

67. Distinguish between polar and nonpolar covalent bonds.
68. ● Why is an HCl molecule polar but a Cl_2 molecule is nonpolar?
69. How does one predict that the chemical bonding between two elements is likely to be ionic?
70. Using just a periodic table (not a table of electronegativities), decide which of these is likely to be the most polar bond. Explain your answer. (a) C--F ; (b) S--F ; (c) Si--F ; (d) O--F .
71. ● Ionic compounds generally have a higher melting point than covalent compounds. What is the major difference in the structures of ionic and covalent compounds that explains the difference in melting points?
72. ● Explain why the electrons in the carbon–fluorine covalent bond tend to move more toward the halogen atom than do the electrons in the carbon–bromine covalent bond.
73. ● Why do we show only partial charges, and not full charges, on the atoms of a polar molecule?
74. In each pair of bonds, indicate the more polar bond, and use δ^+ and δ^- to show the direction of polarity in each bond. (a) C--O and C--N ; (b) N--Cl and C--S ; (c) P--H and P--N ; (d) B--H and B--I .
75. ● The molecule below is urea, a compound used in plastics and fertilizers. (a) Which bonds in this molecule are polar and which are nonpolar? (b) Which is the most polar bond in the molecule? Which atom is the partial negative end of this bond?

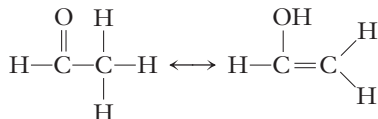


76. (a) Which two of the following pairs of elements are most likely to form ionic bonds? I and H; C and F; Ba and F; N and F; K and O. (b) Of the remaining three pairs, which one forms the least polar, and which the most polar covalent bond?

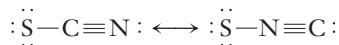
77. (a) List three reasonably nonpolar covalent bonds between dissimilar atoms. (b) List three pairs of elements whose compounds should exhibit extreme ionic character.
78. Classify the bonding between the following pairs of atoms as ionic, polar covalent, or nonpolar covalent. (a) K and O; (b) Br and I; (c) Na and H; (d) O and O; (e) H and O.
79. For each of the following, tell whether the bonding is primarily ionic or covalent. (a) sodium and iodine in sodium iodide; (b) beryllium and the nitrate ion in beryllium nitrate; (c) the carbon-carbon bond in CH_3CH_3 ; (d) carbon and oxygen in carbon monoxide; (e) phosphorus and oxygen in the phosphate ion.
80. Identify the bond in each of the following bonded pairs that is likely to have the greater proportion of "ionic character." (a) Na—Cl or Mg—Cl; (b) Ca—S or Fe—S; (c) Al—Br or O—Br; (d) Ra—H or C—H.
81. Identify the bond in each of the following bonded pairs that is likely to have the greater proportion of "covalent character." (a) K—Br or Cr—Br; (b) Li—O or H—O; (c) Al—Cl or C—Cl; (d) As—S or O—S.
87. If one uses the atomic radii given in Figure 5-1 to calculate the bond length of H—C, H—N, and H—O bonds, do the calculated values agree with those found in Table 7-4? Is the trend for bond length consistent with the location of the elements in the periodic table?
88. Within Table 7-4 is there any indication that there is a trend of bond lengths becoming longer as the group members become larger as one moves down in the periodic table?
89. A monatomic cation most often has a charge of $1+$, $2+$, or $3+$. A monatomic anion most often has a charge of $1-$, $2-$, or $3-$. Consider all the possible combinations of a monatomic cation (M^+ , M^{2+} , or M^{3+}) with a monatomic anion (X^- , X^{2-} , or X^{3-}). How many possible combinations are there? What would be the simplest formula for a neutral compound made by each of these combinations? Are any of the formulas the same? Altogether, how many different simplest formulas, produced from these combinations, are there?
90. It is often assumed that when a metal combines with a nonmetal, the compound produced is ionic. Alternately, if the electronegativity difference between two elements is large, the compound they form is likely to be ionic. But the ultimate test is to experimentally examine the properties of the compound produced: Does it *behave* like an ionic compound? Compare the general characteristics of ionic and covalent compounds with the specific properties of the following metal/nonmetal compounds. Do they appear to be ionic or covalent?

Conceptual Exercises

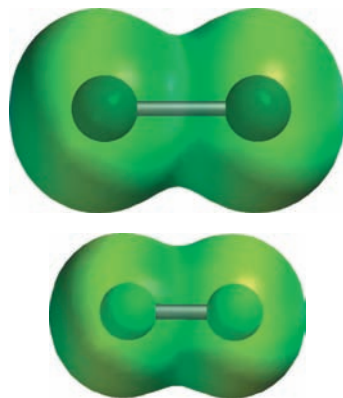
82. When asked to give an example of resonance structures, a student drew the following. Why is this example incorrect?



83. Why is the following not an example of resonance structures?



84. Describe the circumstances under which one would expect a bond to exhibit 100% "covalent character" and 0% "ionic character." Give an example of two bonded atoms that would be predicted to exhibit 0% "ionic character."
85. Select one of the electrostatic charge potential (ECP) plots of a heteronuclear, diatomic molecule found in this chapter. Does the ECP plot that you selected reflect what you have learned thus far in this textbook about atomic size and electronegativity?
86. Below are electrostatic charge potential (ECP) plots for Cl_2 and F_2 . Which one is for Cl_2 ? How can you tell?



	Color	Density (g/cm ³)	Melting point (°C)	Boiling point (°C)	Solubility in H ₂ O (g/100 cm ³)
SnCl ₂	white	3.95	246	623	83.9
SnCl ₄	colorless	2.23	-33	114	decomposes
SnBr ₂	yellow	5.12	216	620	85
SnBr ₄	white	3.34	31	202	very soluble
SnI ₂	red	5.28	320	714	0.99
SnI ₄	red-orange	4.56	143	364	decomposes
PbCl ₂	white	5.85	501	950	0.99
PbCl ₄	yellow	3.18	-15	50	decomposes

What difference does the charge on the metal ion appear to have on the type of compound formed?

Building Your Knowledge

91. (a) How many moles of electrons are transferred when 10.0 g of magnesium react as completely as possible with 10.0 g of fluorine to form MgF_2 ? (b) How many electrons is this? (c) Look up the charge on the electron in coulombs. What is the total charge, in coulombs, that is transferred?

92. Write the formula for the compound that forms between (a) calcium and nitrogen; (b) aluminum and oxygen; (c) potassium and selenium; and (d) strontium and bromine. Classify each compound as covalent or ionic.
93. Write the Lewis formulas for the nitric acid molecule (HNO_3) that are consistent with the following bond length data: 1.405 Å for the bond between the nitrogen atom and the oxygen atom that is attached to the hydrogen atom; 1.206 Å for the bonds between the nitrogen atom and each of the other oxygen atoms.



Charles D. Winters

Aqueous nitric acid solution

94. Write the total ionic and net ionic equations for the reaction between each of the following pairs of compounds in aqueous solution. Then give the Lewis formula for each species in these equations. (a) HCN and NaOH ; (b) HCl and NaOH ; (c) CaCl_2 and Na_2CO_3 .
95. Sketch a portion of an aqueous solution of NaCl . Show the Lewis formulas of the solute and solvent species. Suggest the relative location of each species with respect to the others.
96. Sketch a portion of an aqueous solution of CH_3COOH . Show the Lewis formulas of the solute and solvent species. Suggest the relative location of each species with respect to the others.
97. The following properties can be found in the *Handbook of Chemistry and Physics*:
Camphor, $\text{C}_{10}\text{H}_{16}\text{O}$ — colorless crystals; specific gravity, 0.990 at 25 °C; sublimes, 204 °C; insoluble in water; very soluble in alcohol and ether.
Praseodymium chloride, PrCl_3 — blue-green needle crystals; specific gravity, 4.02; melting point, 786 °C; boiling point, 1700 °C; solubility in cold water, 103.9 g/100 mL H_2O ; very soluble in hot water. Would you describe each of these as ionic or covalent? Why?

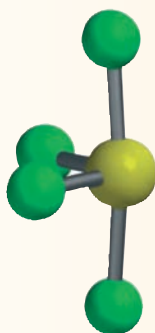
Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

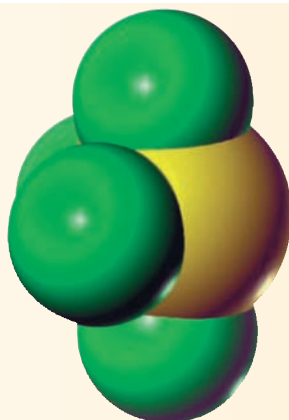
98. Look up the properties of NaCl and PCl_3 in the *Handbook of Chemistry and Physics*. Why do we describe NaCl as an ionic compound and PCl_3 as a covalent compound?
99. Look up the dipole moment for CO (carbon monoxide). How does it compare to the formal charges calculated from the Lewis dot structure? What does that tell you about the physical meaning of formal charges for this molecule? How does the dipole moment fit with electronegativity values for the atoms?
100. CO_2 does not have a dipole moment and is considered a nonpolar molecule. CO_2 readily reacts with water and hydroxide ions. What two compounds are formed? Sketch out Lewis dot structures for these two compounds.
101. Use the *Handbook of Chemistry and Physics* or a suitable web page to find dipole moments. Do the values for HF , HCl , and HI agree with what you also know about electronegativity?

Molecular Structure and Covalent Bonding Theories

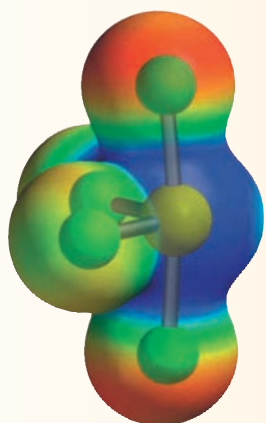
8



A Ball-and-stick model

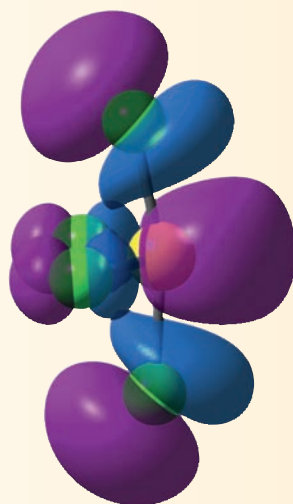


B Space-filling model



δ^-  δ^+

C Ball-and-stick model with electrostatic charge potential surface showing relative charges on the atoms



D Highest energy molecular orbital showing the lone pair orbital on the sulfur atom and the fluorine *p*-orbitals

Some representations of the structure and bonding in SF_4 . Refer to Example 7-7 for Lewis formula.

OUTLINE

- 8-1 A Preview of the Chapter
- 8-2 Valence Shell Electron Pair Repulsion Theory
- 8-3 Polar Molecules: The Influence of Molecular Geometry
- 8-4 Valence Bond Theory
- Molecular Shapes and Bonding**
- 8-5 Linear Electronic Geometry: AB_2 Species (No Lone Pairs on A)
- 8-6 Trigonal Planar Electronic Geometry: AB_3 Species (No Lone Pairs on A)
- 8-7 Tetrahedral Electronic Geometry: AB_4 Species (No Lone Pairs on A)
- 8-8 Tetrahedral Electronic Geometry: AB_3U Species (One Lone Pair on A)
- 8-9 Tetrahedral Electronic Geometry: AB_2U_2 Species (Two Lone Pairs on A)
- 8-10 Tetrahedral Electronic Geometry: ABU_3 Species (Three Lone Pairs on A)
- 8-11 Trigonal Bipyramidal Electronic Geometry: AB_5 , AB_4U , AB_3U_2 , and AB_2U_3
- 8-12 Octahedral Electronic Geometry: AB_6 , AB_5U , and AB_4U_2
- 8-13 Lone Pairs on the Central Atom—A Summary
- 8-14 Compounds Containing Double Bonds
- 8-15 Compounds Containing Triple Bonds
- 8-16 A Summary of Electronic and Molecular Geometries

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Describe the basic ideas of the valence shell electron pair repulsion (VSEPR) theory
- ▶ Use the VSEPR theory to predict the electronic geometry and the molecular geometry of polyatomic molecules and ions
- ▶ Describe the relationships between molecular shapes and polarities
- ▶ Predict whether a molecule is polar or nonpolar
- ▶ Describe the basic ideas of the valence bond (VB) theory
- ▶ Describe the hybrid orbitals used in bonding in polyatomic molecules and ions
- ▶ Use the theory of hybrid orbitals to describe the bonding in double and triple bonds

We know a great deal about the molecular structures of millions of compounds, all based on reliable experiments. In our discussion of theories of covalent bonding, we must keep in mind that the theories represent *an attempt to explain and organize* what we know. For bonding theories to be valid, they must be consistent with the large body of experimental observations about molecular structure. In this chapter we will study two theories of covalent bonding. These theories allow us to predict correct structures and properties. Like any simplified theories, they are not entirely satisfactory in describing *every* known structure; however, their successful application to the vast majority of structures studied justifies their continued use.

8-1 A Preview of the Chapter

The electrons responsible for bonding are those in the outer shell, or **valence shell**, of an atom. Valence shell electrons are those that were not present in the *preceding* noble gas orbitals. We will focus attention on these electrons in our discussion of covalent bonding. The electrons in the lower energy noble gas configuration are not directly involved in covalent bonding and are often referred to as *core electrons*. Lewis formulas show the number of valence shell electrons in a polyatomic molecule or ion (see Sections 7-5 through 7-9). We will write Lewis formulas for each molecule or polyatomic ion we discuss. The theories introduced in this chapter apply equally well to polyatomic molecules and to ions.

Two theories go hand in hand in a discussion of covalent bonding. The *valence shell electron pair repulsion (VSEPR) theory* predicts the spatial arrangement of atoms in a polyatomic molecule or ion. It shows *where* the bonding occurs and where lone (unshared) pairs of valence shell electrons are directed, but it does not explain *how* the bonding occurs. The *valence bond (VB) theory* describes *how* the bonding takes place, in terms of *overlapping atomic orbitals*. In this theory, the atomic orbitals discussed in Chapter 4 are often “mixed,” or *hybridized*, to form new orbitals with different spatial orientations. Used together, these two simple ideas enable us to understand the bonding, molecular shapes, and properties of a wide variety of polyatomic molecules and ions.

We will first discuss the basic ideas and application of these two theories. Then we will learn how the important molecular property of *polarity* depends on molecular shape. Most of this chapter will then be devoted to studying how these ideas are applied to various types of polyatomic molecules and ions.

Important Note

Different instructors prefer to cover these two theories in different ways. Your instructor will tell you the order in which you should study the material in this chapter. Regardless of how you study this chapter, Tables 8-1, 8-2, 8-3, and 8-4 are important summaries, and you should refer to them often.

1. One approach is to discuss both the VSEPR theory and the VB theory together, emphasizing how they complement each other. If your instructor prefers this parallel approach, you should study the chapter in the order in which it is presented.

▶ Lone pairs are sometimes called unshared pairs.

▶ In Chapter 7 we used valence bond terminology to discuss the bonding in H_2 , although we did not name the theory there.

2. An alternative approach is to first master the VSEPR theory and the related topic of molecular polarity for different structures, and then learn how the VB theory describes the overlap of bonding orbitals in these structures. If your instructor takes this approach, you should study this chapter in the following order:
 - a. Read the summary material under the main heading “Molecular Shapes and Bonding” preceding Section 8-5.
 - b. *VSEPR theory, molecular polarity*. Study Sections 8-2 and 8-3; then in Sections 8-5 through 8-12, study only the subsections marked A and B.
 - c. *VB theory*. Study Section 8-4; then in Sections 8-5 through 8-13, study the Valence Bond Theory subsections, marked C; then study Sections 8-14 and 8-15.

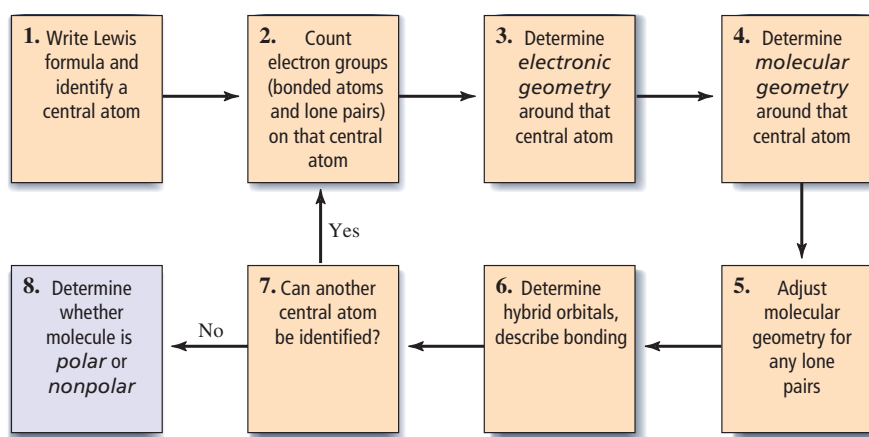
No matter which order your instructor prefers, the following procedure will help you analyze the structure and bonding in any compound.

1. Write the Lewis formula for the molecule or polyatomic ion, and identify a *central atom*—an atom that is bonded to more than one other atom (Section 8-2).
2. Count the *number of electron groups* (bonded atoms and lone pairs) on the central atom (Section 8-2).
3. Apply the VSEPR theory to determine the arrangement of the *electron groups* (the *electronic geometry*) about the central atom (Section 8-2; Tables 8-1 and 8-4).
4. Using the Lewis formula as a guide, determine the arrangement of the *bonded atoms* (the *molecular geometry*) about the central atom, as well as the location of the lone pairs on that atom (Parts B of Sections 8-5 through 8-12; Tables 8-3 and 8-4). This description includes ideal bond angles.
5. If there are lone pairs of valence shell electrons on the central atom, consider how their presence might modify somewhat the *ideal* molecular geometry and bond angles deduced in Step 4 (Section 8-2; Parts B of Sections 8-8 and 8-9; Parts D of Sections 8-11 and 8-12).
6. Use the VB theory to determine the *hybrid orbitals* utilized by the central atom; describe the overlap of these orbitals to form bonds; describe the orbitals that contain lone pairs of valence shell electrons on the central atom (Parts C of Sections 8-5 through 8-12; Sections 8-14 and 8-15; Tables 8-2, 8-3, and 8-4).
7. If more than one atom can be identified as a central atom (as in many organic molecules), repeat Steps 2 through 6 for each central atom, to build up a picture of the geometry and bonding in the entire molecule or ion.
8. When all central atoms in the molecule or ion have been accounted for, use the entire molecular geometry, electronegativity differences, and the presence of lone pairs of valence shell electrons on the central atom to predict *molecular polarity* (Section 8-3; Parts B of Sections 8-5 through 8-12; Section 8.13).

STOP & THINK

Never skip to Step 4 until you have done Step 3. The electronic geometry and the molecular geometry may or may not be the same; knowing the electronic geometry first will enable you to determine the correct molecular geometry.

The following diagram summarizes this procedure.



STOP & THINK

Learn this procedure, and use it as a mental “checklist.” Trying to do this reasoning in a different order often leads to confusion or wrong answers.

STOP & THINK

Remember to take into account the “extra” electrons on anions and the “missing” electrons for cations.

In Section 7-5 we showed that Lewis formulas of polyatomic ions can be constructed in the same way as those of neutral molecules. Once the Lewis formula of an ion is known, we use the VSEPR and VB theories to deduce its electronic geometry, shape, and hybridization, just as for neutral molecules.

8-2 Valence Shell Electron Pair Repulsion Theory

The basic ideas of the **valence shell electron pair repulsion (VSEPR) theory** are:

Each region of high electron density in the valence shell of a central atom is significant. Such a region is referred to as an *electron group*. The groups of valence shell electrons on the *central atom* repel one another. They are arranged about the *central atom* so that the repulsions among them are as small as possible. This results in maximum separation of the electron groups about the central atom.

A **central atom** is any atom that is bonded to more than one other atom. We first count the number of **electron groups** around the *central atom*, as follows:

1. Each bonded atom is counted as *one electron group* for VSEPR, *regardless of whether the bonding is single, double, or triple*.
2. Each lone pair of valence electrons on the central atom is counted as *one electron group* for VSEPR.

► The VSEPR theory assumes that the electron groups (which are regions of high electron density on the central atom) will be as far from one another as possible.

The number of electron groups then determines their arrangement around that central atom. In some molecules, more than one central atom may be present. In such a case, we determine the arrangement around each central atom in turn, to build up a picture of the overall shape of the entire molecule or ion.

Consider the following molecules and polyatomic ions as examples.

Formula:	CO ₂	NH ₃	CH ₄	NO ₃ ⁻
Lewis formula:	$\text{:}\ddot{\text{O}}=\text{C}=\ddot{\text{O}}\text{:}$	$\begin{array}{c} \text{H} \\ \\ \text{N}-\text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$\left[\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ \\ \text{:}\ddot{\text{O}}-\text{N}-\ddot{\text{O}}\text{:} \\ \diagup \quad \diagdown \\ \text{:}\ddot{\text{O}}\text{:} \quad \text{:}\ddot{\text{O}}\text{:} \end{array} \right]^{-}$
Central atom:	C	N	C	N
Number of atoms bonded to <i>central atom</i> :	2	3	4	3
Number of lone pairs on <i>central atom</i> :	0	1	0	0
Total number of electron groups on <i>central atom</i> :	2	4	4	3

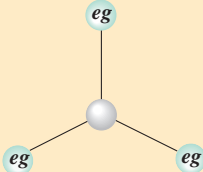
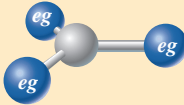
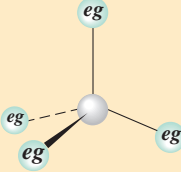
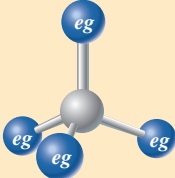
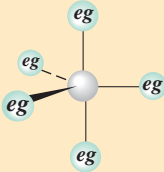
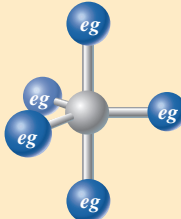
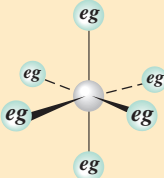
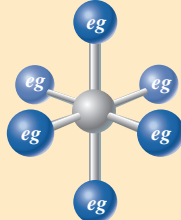
STOP & THINK

Note that each oxygen atom is counted as a single electron group, regardless of whether there is a single or double bond present. When you count atoms bonded to the central atom, do not consider the number of bonds between those atoms.

According to VSEPR theory, the molecule or ion is most stable when the electron groups on the central atom are as far apart as possible. The arrangement of these *electron groups* around the central atom is referred to as the **electronic geometry** of the central atom.

For instance, two electron groups are most stable on opposite sides of the central atom (the linear arrangement), where they repel one another as little as possible. Three regions are most stable when they are arranged at the corners of an equilateral triangle. Table 8-1

Table 8-1 Electronic Geometry versus Number of Electron Groups (eg) on Central Atom

Electron Groups on Central Atom	Electronic Geometry*			Ball-and-Stick Model
	Orientation of Electron Groups	Description; Angles [†]	Line Drawing [‡]	
2		linear; 180°		
3		trigonal planar; 120°		
4		tetrahedral; 109.5°		
5		trigonal bipyramidal; 90°, 120°, 180°		
6		octahedral; 90°, 180°		

*Electronic geometries are illustrated here using electron groups (“eg”) that represent lone pairs or bonded atoms about the central atom (gray sphere). In the ball-and-stick models the electron groups are located at the end of the silver sticks (atoms) or in the region of space around the silver stick (lone pairs).

[†]Angles made by imaginary lines through the nucleus and the electron groups.

[‡]By convention, a line in the plane of the drawing is represented by a solid line —, a line behind this plane is shown as a dashed line ----, and a line in front of this plane is shown as a wedge — with the fat end of the wedge nearest the viewer. Chemists also use a dashed wedge (—) to indicate an atom oriented behind the plane or atom to which it is bonded.

shows the relationship between the common numbers of electron groups and their corresponding electronic geometries. After we know the electronic geometry (and *only then*), we can use the bonding electron groups on the central atom to attach the remaining atoms. This lets us deduce the arrangement of *atoms* around the central atom, called the **molecular geometry**. If necessary, we repeat this procedure for each central atom in the molecule or ion. These procedures are illustrated in Parts B of Sections 8-5 through 8-12.

► You must know the electronic geometry before you can deduce the molecular geometry.

Unless otherwise noted, all content on this page is © Cengage Learning.

8-3 Polar Molecules: The Influence of Molecular Geometry

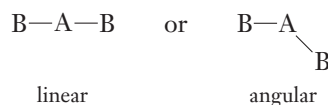
In Chapter 7 we saw that the unequal sharing of electrons between two atoms with different electronegativities, $\Delta(\text{EN}) > 0$, results in a *polar bond*. For heteronuclear diatomic molecules such as HF, this bond polarity results in a *polar molecule*. Then the entire molecule acts as a dipole, and we would find that the molecule has a measurable *dipole moment*, that is, it is greater than zero.

When a molecule consists of more than two atoms joined by polar bonds, we must also take into account the *arrangement* of the resulting bond dipoles to decide whether or not a molecule is polar. For such a case, we first use the VSEPR theory to deduce the molecular geometry (arrangement of atoms), as described in the preceding section and exemplified in Parts A and B of Sections 8-5 through 8-12. Then we determine whether the bond dipoles are arranged in such a way that they cancel (so that the resulting molecule is *nonpolar*) or do not cancel (so that the resulting molecule is *polar*).

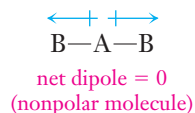
In this section we will discuss the ideas of cancellation of dipoles in general terms, using general atomic symbols A and B. Then we will apply these ideas to specific molecular geometries and molecular polarities in Parts B of Sections 8-5 through 8-12.

Let us consider a heteronuclear triatomic molecule with the formula AB_2 (A is the central atom). Such a molecule must have one of the following two molecular geometries:

► The angular form could have different angles, but either the molecule is linear or it is not. The angular arrangement is sometimes called *V-shaped* or *bent*.



Suppose that atom B has a higher electronegativity than atom A. Then each A—B bond is polar, with the negative end of the bond dipole pointing toward B. We can view each bond dipole as an *electronic vector*, with a *magnitude* and a *direction*. In the linear AB_2 arrangement, the two bond dipoles are *equal* in magnitude and *opposite* in direction. They therefore cancel to give a nonpolar molecule (dipole moment equal to zero).

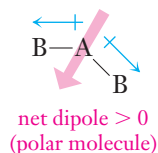


In the case of the angular arrangement, the two equal dipoles *do not cancel*, but add to give a dipole moment greater than zero. The angular molecular arrangement represents a polar molecule.

► In this chapter the direction of the net dipole is indicated by a shaded arrow:



The arrow head indicates the area of partial negative charge and the tail (without a cross) represents the region of partial positive charge.



If the electronegativity differences were reversed in the $\text{B}-\text{A}-\text{B}$ molecule—that is, if A were more electronegative than B—the directions of all bond polarities would be reversed. But the bond polarities would still cancel in the linear arrangement to give a nonpolar molecule. In the angular arrangement, bond polarities would still add to give a polar molecule, but with the net dipole pointing in the opposite direction from that described earlier.

We can make similar arguments based on addition of bond dipoles for other arrangements. As we will see in Section 8-8, lone pairs on the central atom can also affect the direction and the magnitude of the net molecular dipole, so the presence of lone pairs on the central atom must always be taken into account.

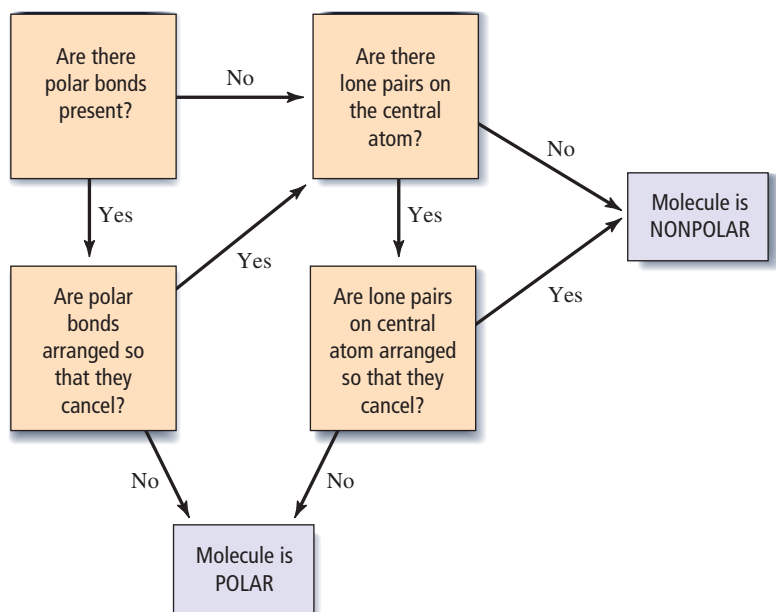


Figure 8-1 A guide to determining whether a polyatomic molecule is polar or nonpolar. Study the more detailed presentation in the text.

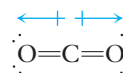
For a molecule to be polar, *two* conditions must *both* be met:

1. There must be at least one polar bond or one lone pair on the central atom.
and
2. a. The polar bonds, if there are more than one, must be arranged so that their polarities (bond dipoles) *do not cancel*.
or
b. If there are two or more lone pairs on the central atom, they must be arranged so that their polarities *do not cancel*.

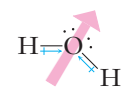
Put another way, if there are no polar bonds or lone pairs of electrons on the central atom, the molecule *cannot* be polar. Even if polar bonds or lone pairs are present, they may be arranged so that their polarities cancel one another, resulting in a nonpolar molecule.

Carbon dioxide, CO_2 , is a three-atom molecule in which each carbon-oxygen bond is *polar* because of the electronegativity difference between C and O. But the molecule *as a whole* is shown by experiment (dipole moment measurement) to be nonpolar. This tells us that the polar bonds are arranged in such a way that the bond polarities cancel. Water, H_2O , on the other hand, is a very polar molecule; this tells us that the H—O bond polarities do not cancel one another. Molecular shapes clearly play a crucial role in determining molecular dipole moments. We will develop a better understanding of molecular shapes in order to understand molecular polarities.

The logic used to predict whether a molecule is polar or nonpolar is outlined in Figure 8-1. The approach described in this section will be applied to various electronic and molecular geometries in Parts B of Sections 8-5 through 8-12.



linear molecule;
bond dipoles cancel;
molecule is nonpolar



angular molecule;
bond dipoles do not cancel;
molecule is polar

8-4 Valence Bond Theory

In Chapter 7 we described covalent bonding as electron pair sharing that results from the overlap of orbitals from two atoms. This is the basic idea of the **valence bond (VB) theory**—it describes *how* bonding occurs. In many examples throughout this chapter, we first use the VSEPR theory to describe the *orientations* of the electron



We can describe hybridization as the mathematical combination of the waves that represent the orbitals of the atom. This is analogous to the formation of new waves on the surface of water when different waves interact.

► Although the terminology is not as precise as we might wish, we use “molecular geometry” to describe the arrangement of atoms in *polyatomic ions* as well as in molecules.

groups. Then we use the VB theory to describe the atomic orbitals that overlap to produce the bonding with that geometry. We also assume that each lone pair occupies a separate orbital. Thus, the two theories work together to give a fuller description of the bonding.

We learned in Chapter 4 that an isolated atom has its electrons arranged in orbitals in the way that leads to the lowest total energy for the atom. Usually, however, these “pure atomic” orbitals do not have the correct energies or orientations to describe where the electrons are when an atom is bonded to other atoms. When other atoms are nearby as in a molecule or ion, an atom can combine its valence shell orbitals to form a new set of orbitals that is at a lower total energy in the presence of the other atoms than the pure atomic orbitals would be. This process is called **hybridization**, and the new orbitals that are formed are called **hybrid orbitals**. These hybrid orbitals can overlap with orbitals on other atoms to share electrons and form bonds. Such hybrid orbitals *usually* give an improved description of the experimentally observed geometry of the molecule or ion. In fact, the concept of hybrid orbitals was developed specifically to explain the geometries of polyatomic ions and molecules.

The designation (label) given to a set of hybridized orbitals reflects the *number and kind* of atomic orbitals that hybridize to produce the new set (Table 8-2). Further details about hybridization and hybrid orbitals appear in the following sections. Throughout the chapter, hybrid orbitals are shaded in green, while atomic orbitals are colored blue.

Molecular Shapes and Bonding

STOP & THINK

See the “Important Note” on page 288 in Section 8-1; consult your instructor for guidance on the order in which you should study Sections 8-5 through 8-12.

We are now ready to study the structures of some simple molecules. We often refer to generalized chemical formulas in which “A” represents the central atom and “B” represents an atom bonded to A. We follow the eight steps of analysis outlined in Section 8-1. We first give the known (experimentally determined) facts about the polarity and the shape of the molecule. We then write the Lewis formula (Part A of each section). Then we explain these facts in terms of the VSEPR and VB theories. The simpler VSEPR theory will be used to explain (or predict) first the *electronic geometry* (all the electron groups) and then the *molecular geometry* (just the bonded atoms) in the molecule (Part B). We then show how the molecular polarity of a molecule is a result of bond polarities, lone pairs, and molecular geometry. Finally, we use the VB theory to describe the bonding in molecules in more detail, usually using hybrid orbitals (Part C). As you study each section, refer frequently to the summaries that appear in Table 8-4.

Table 8-2 Relation Between Electronic Geometries and Hybridization

Electron Groups on Central Atom	Electronic Geometry	Atomic Orbitals Mixed from Valence Shell of Central Atom	Hybridization
2	linear	one <i>s</i> , one <i>p</i>	<i>sp</i>
3	trigonal planar	one <i>s</i> , two <i>p</i> 's	<i>sp</i> ²
4	tetrahedral	one <i>s</i> , three <i>p</i> 's	<i>sp</i> ³
5	trigonal bipyramidal	one <i>s</i> , three <i>p</i> 's, one <i>d</i>	<i>sp</i> ³ <i>d</i>
6	octahedral	one <i>s</i> , three <i>p</i> 's, two <i>d</i> 's	<i>sp</i> ³ <i>d</i> ²

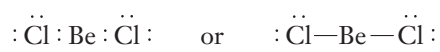
8-5 Linear Electronic Geometry: AB₂ Species (No Lone Pairs on A)

A. Experimental Facts and Lewis Formulas

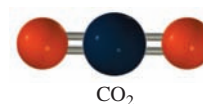
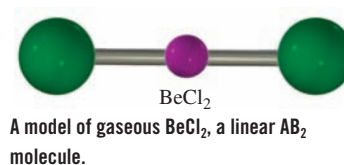
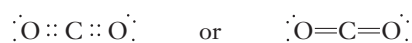
Several linear molecules consist of a central atom plus two atoms of another element, abbreviated as AB₂. These compounds include BeCl₂, BeBr₂, and BeI₂ (in their gaseous state), as well as CdX₂ and HgX₂, where X = Cl, Br, or I. All of these are known to be linear (bond angle = 180°), nonpolar, covalent compounds.

Let's focus on *gaseous* BeCl₂ molecules. We wrote the Lewis formula for BeCl₂ in Example 7-4. It shows two single covalent bonds, with Be and Cl each contributing one electron to each bond.

In many of its compounds, Be does not satisfy the octet rule (see Section 7-8).

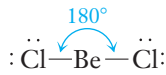


Another linear, nonpolar AB₂ molecule is carbon dioxide, CO₂.

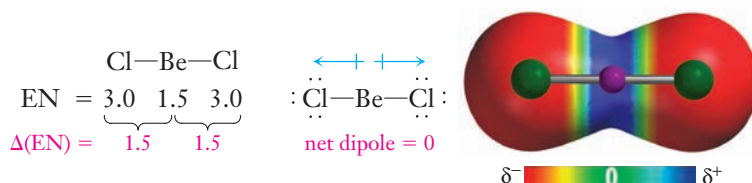


B. VSEPR Theory

Valence shell electron pair repulsion theory places the two electron pairs on Be 180° apart, that is, with **linear electronic geometry**. Both electron pairs are bonding pairs, so VSEPR also predicts a linear atomic arrangement, or *linear molecular geometry*, for BeCl₂.



If we examine the bond dipoles, we see that the electronegativity difference (see Table 5-3) is large (1.5 units) and each bond is quite polar:



The two bond dipoles are *equal* in magnitude and *opposite* in direction. They therefore cancel to give a nonpolar molecule.

The difference in electronegativity between Be and Cl is so large that we might expect ionic bonding. The radius of Be²⁺ is so small (0.59 Å) and its *charge density* (ratio of charge to size) is so high, however, that most simple beryllium compounds are covalent rather than ionic. The high charge density of Be²⁺ causes it to attract and distort the electron cloud of monatomic anions of all but the most electronegative elements. As a result, the bonds in BeCl₂ are polar covalent rather than ionic. Two exceptions are BeF₂ and BeO. They are ionic compounds because they contain the two most electronegative elements bonded to Be.

Similarly, VSEPR theory counts two electron groups on the carbon atom in CO₂. Thus, C in CO₂ has linear electronic geometry with both electron groups attached to O atoms. The molecular geometry of CO₂ is linear. Each C=O bond is polar, but these

► The VSEPR theory describes the locations of bonded atoms around the central atom, as well as where its lone pairs of valence shell electrons are directed.

STOP & THINK

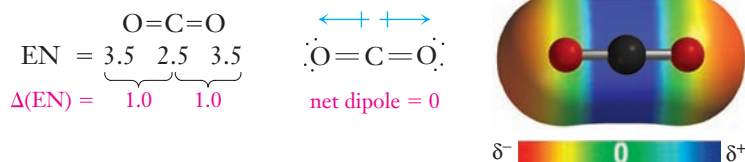
It is important to distinguish between *nonpolar bonds* and *nonpolar molecules*. Polar bonds do not necessarily produce a polar molecule.

► We say that the Be²⁺ ion *polarizes* the anions, Cl⁻.

STOP & THINK

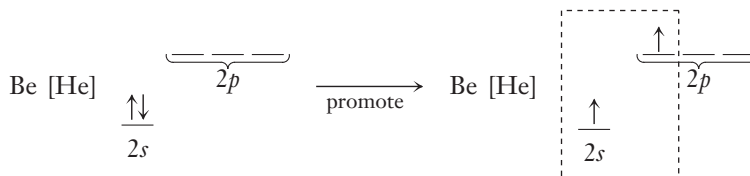
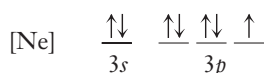
Remember that a double bond counts as only one electron group.

bond dipoles point in opposite directions (180°), so they cancel, making CO_2 a nonpolar molecule.

**C. Valence Bond Theory**

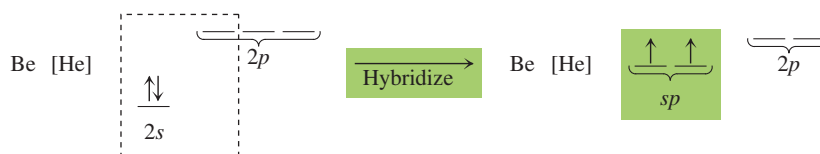
Consider the ground state electron configuration of Be. There are two electrons in the $1s$ orbital, but these nonvalence (inner or *core*) electrons are *not* involved in bonding. Two more electrons are *paired* in the $2s$ orbital. How, then, will a Be atom bond to two Cl atoms? The Be atom must somehow make available one orbital for each bonding Cl electron (the unpaired p electrons). The following *ground state* electron configuration for Be is the configuration for an isolated Be atom. Another configuration may be more stable when the Be atom is covalently bonded. Suppose that the Be atom “promoted” one of the paired $2s$ electrons to one of the $2p$ orbitals, the next higher energy orbitals.

► Cl ground state configuration:



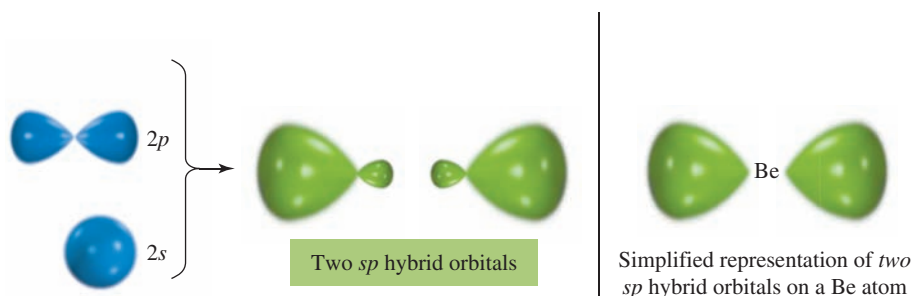
Then there would be two Be orbitals available for bonding. This description, however, is still not fully consistent with experimental fact. The Be $2s$ and $2p$ orbitals could not overlap a Cl $3p$ orbital with equal effectiveness; that is, this “promoted pure atomic” arrangement would predict two *nonequivalent* Be—Cl bonds. Yet we observe experimentally that the Be—Cl bonds are *identical* in bond length and strength.

For these two different orbitals on Be to become equivalent, they must *hybridize* to give two new orbitals that reflect the equal contribution of the s and p orbitals. These are called ***sp* hybrid orbitals**. Consistent with Hund’s Rule, each of these equivalent hybrid orbitals on Be would contain one electron.

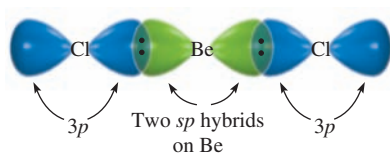


The *sp* hybrid orbitals are described as *linear orbitals*, and we say that Be has *linear electronic geometry*.

► In this chapter, pure atomic orbitals are shown in blue, and hybrid orbitals are shown in green. As we did for pure atomic orbitals, we often draw hybrid orbitals more slender than they actually are. Such drawings are intended to remind us of the orientations and general shapes of orbitals.



We can imagine that there is one electron in each of these hybrid orbitals on the Be atom. Recall that each Cl atom has a half-filled $3p$ orbital that can overlap with a half-filled sp hybrid of Be. We picture the bonding in BeCl_2 in the following diagram, in which only the bonding electrons are represented.



► Lone pairs of electrons on Cl atoms are not shown. The hybrid orbitals on the central atom are shown in green in this and subsequent drawings. The atomic orbitals are shown all in blue without different phase colors.

Thus, the Be and two Cl nuclei would lie on a straight line. *This is consistent with the experimental observation that the molecule is linear.*

The structures of beryllium bromide, BeBr_2 , and beryllium iodide, BeI_2 , are similar to that of BeCl_2 . The chlorides, bromides, and iodides of cadmium, CdX_2 , and mercury, HgX_2 , are also linear covalent molecules (where $\text{X} = \text{Cl}, \text{Br}, \text{or I}$).

► The two X's within one structure are identical.

When there are two electron groups around the central atom, it is sp hybridized. AB_2 molecules and ions with no lone pairs on the central atom have linear electronic geometry, linear molecular geometry, and sp hybridization on the central atom.

The linear geometry of carbon in CO_2 tells us that the hybridization on the carbon is sp . We will postpone a detailed discussion of the double bonds until Section 8-14.

Problem-Solving Tip

Number and Kind of Hybrid Orbitals

One additional idea about hybridization is worth special emphasis:

The number of hybrid orbitals is always equal to the number of atomic orbitals that hybridize.

Hybrid orbitals are named by indicating the *number and kind* of atomic orbitals hybridized. Hybridization of *one s* orbital and *one p* orbital gives *two sp hybrid orbitals*. We shall see presently that hybridization of *one s* and *two p* orbitals gives *three sp² hybrid orbitals*; hybridization of *one s* orbital and *three p* orbitals gives *four sp³ hybrids*, and so on (see Table 8-2).

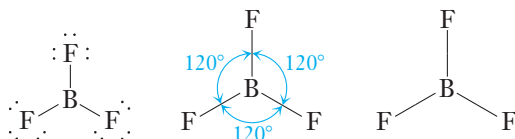
► Hybridization usually involves orbitals from the same main shell (same n).

8-6 Trigonal Planar Electronic Geometry: AB₃ Species (No Lone Pairs on A)

A. Experimental Facts and Lewis Formulas

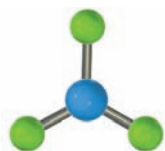
Boron is a Group 3A element that forms many covalent compounds by bonding to three other atoms. Typical examples include boron trifluoride, BF_3 (mp = -127°C); boron trichloride, BCl_3 (mp = -107°C); boron tribromide, BBr_3 (mp = -46°C); and boron triiodide, BI_3 (mp = 50°C). All are trigonal planar nonpolar molecules.

► A trigonal planar molecule is a flat molecule in which all three bond angles are 120° .

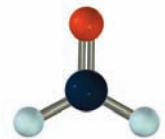


The Lewis formula for BF_3 is derived from the following: (a) each B atom has three electrons in its valence shell and (b) each B atom is bonded to three F (or Cl, Br, I) atoms. In Example 7-5 we wrote the Lewis formula for BCl_3 . Both F and Cl are members of Group 7A, and so the Lewis formulas for BF_3 and BCl_3 should be similar.

Unless otherwise noted, all content on this page is © Cengage Learning.



A model of BF_3 , a trigonal planar AB_3 molecule.



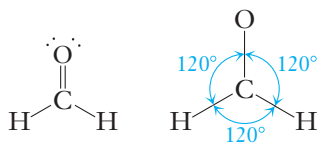
formaldehyde, $\text{H}_2\text{C}=\text{O}$

► Trigonal planar geometry is sometimes called *plane triangular* or simply *triangular*.

► The B^{3+} ion is so small (radius = 0.20 Å) that boron does not form simple ionic compounds.

We see that BF_3 and other similar molecules have a central element that does *not* satisfy the octet rule. Boron shares only six electrons (as do most of the Group 3A elements).

Another trigonal AB_3 molecule is formaldehyde, $\text{H}_2\text{C}=\text{O}$, one of the simplest organic compounds.

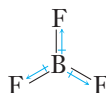


B. VSEPR Theory

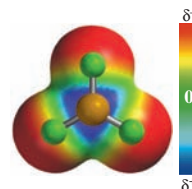
Boron, the central atom, has three electron groups (three bonded atoms, no lone pairs on B). The VSEPR theory predicts **trigonal planar electronic geometry** for molecules such as BF_3 because this structure gives maximum separation among the three electron groups. There are no lone pairs of electrons associated with the boron atom, so a fluorine atom is at each corner of the equilateral triangle, and the *molecular geometry* is also trigonal planar. The maximum separation of any three items (electron groups) around a fourth item (B atom) is at 120° angles in a single plane. All four atoms are in the same plane. The three F atoms are at the corners of an equilateral triangle, with the B atom in the center. The structures of BCl_3 , BBr_3 , and BI_3 are similar.

Examination of the bond dipoles of BF_3 shows that the electronegativity difference (see Table 5-3) is very large (2.0 units) and that the bonds are very polar.

$$\begin{array}{c} \text{B}-\text{F} \\ \text{EN} = \begin{array}{cc} 2.0 & 4.0 \end{array} \\ \Delta(\text{EN}) = \begin{array}{c} \text{ } \\ 2.0 \end{array} \end{array}$$



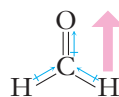
net molecular dipole = 0



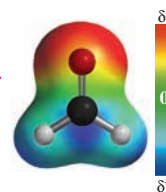
However, the three bond dipoles are symmetrically distributed, so they cancel to give a nonpolar molecule.

Similarly, VSEPR theory counts three electron groups on the carbon atom in $\text{H}_2\text{C}=\text{O}$. Therefore, C in $\text{H}_2\text{C}=\text{O}$ has trigonal planar electronic geometry with the three electron groups bonded to one oxygen and two hydrogen atoms. The molecular geometry of $\text{H}_2\text{C}=\text{O}$ is thus trigonal planar. The $\text{C}=\text{O}$ bond is far more polar than the $\text{C}=\text{H}$ bonds and is the biggest factor in defining the overall dipole of formaldehyde.

$$\begin{array}{c} \text{C}=\text{O} \\ \text{EN} = \begin{array}{cc} 2.5 & 3.5 \end{array} \\ \Delta(\text{EN}) = \begin{array}{c} \text{ } \\ 1.0 \end{array} \end{array} \quad \begin{array}{c} \text{H}-\text{C} \\ \text{EN} = \begin{array}{cc} 2.1 & 2.5 \end{array} \\ \Delta(\text{EN}) = \begin{array}{c} \text{ } \\ 0.4 \end{array} \end{array}$$



net molecular dipole > 0

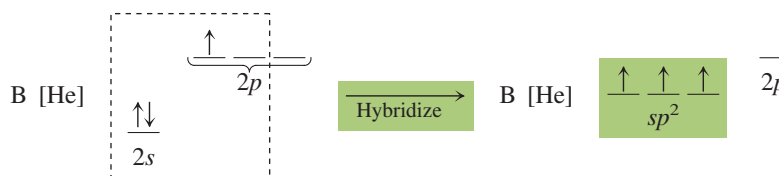


STOP & THINK

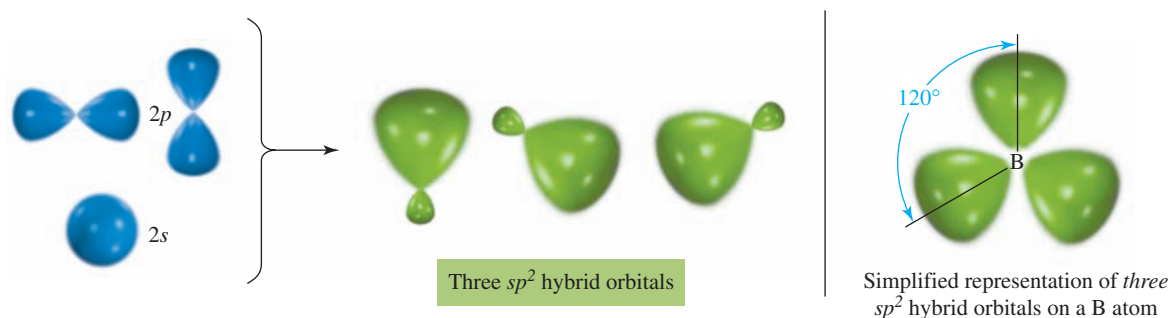
Students often forget that the notation for hybridized orbitals indicates both the number of orbitals used in the hybridization and the number of hybrid orbitals obtained. For example, sp^2 indicates three orbitals.

C. Valence Bond Theory

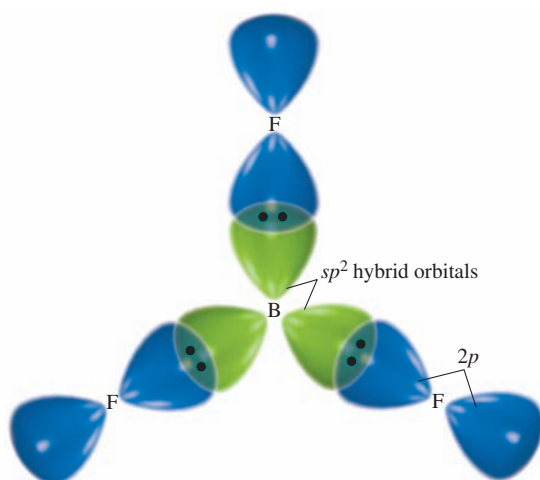
To be consistent with experimental findings and the predictions of the VSEPR theory, the VB theory must explain three *equivalent* $\text{B}-\text{F}$ bonds. Again we use the idea of hybridization. Now the $2s$ orbital and two of the $2p$ orbitals of B hybridize to form a set of three equivalent **sp^2 hybrid orbitals**.



Three sp^2 hybrid orbitals point toward the corners of an equilateral triangle:



The B atom supplies one electron in each of these hybrid orbitals. Each of the three F atoms has a $2p$ orbital with one unpaired electron. The $2p$ orbitals can overlap the three sp^2 hybrid orbitals on B. Three electron pairs are shared among one B and three F atoms:



► Lone pairs of electrons are not shown for the F atoms.

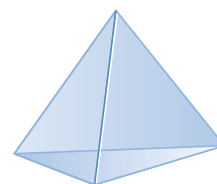
When there are three electron groups around the central atom, it is sp^2 hybridized. AB₃ molecules and ions with no lone pairs on the central atom have trigonal planar electronic geometry, trigonal planar molecular geometry, and sp^2 hybridization on the central atom.

In $\text{H}_2\text{C}=\text{O}$ the trigonal planar geometry on carbon tells us that the hybridization on the carbon is sp^2 . As with CO_2 , we will postpone a detailed discussion of the double bonds until Section 8-14.

8-7 Tetrahedral Electronic Geometry: AB₄ Species (No Lone Pairs on A)

A. Experimental Facts and Lewis Formulas

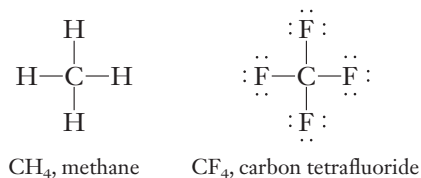
Each Group 4A element has four electrons in its highest occupied energy level. The Group 4A elements form many covalent compounds by sharing those four electrons with four other atoms. Typical examples include CH_4 (mp = -182°C), CF_4 (mp = -184°C), CCl_4 (mp = -23°C), SiH_4 (mp = -185°C), and SiF_4 (mp = -90°C). All are tetrahedral, nonpolar molecules (bond angles = 109.5°). In each, the Group 4A atom is located in the center of a regular tetrahedron. The other four atoms are located at the four corners of the tetrahedron.



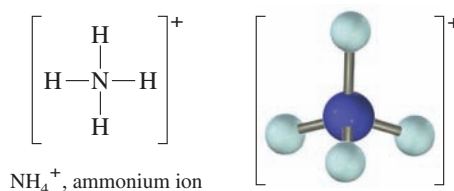
► The names of many solid figures are based on the numbers of plane faces they have. A **regular tetrahedron** is a three-dimensional figure with four equal-sized equilateral triangular faces (the prefix *tetra-* means "four").

Unless otherwise noted, all content on this page is © Cengage Learning.

The Group 4A atom contributes four electrons to the bonding in a tetrahedral AB_4 molecule, and the other four atoms contribute one electron each. The Lewis formulas for methane, CH_4 , and carbon tetrafluoride, CF_4 , are typical.

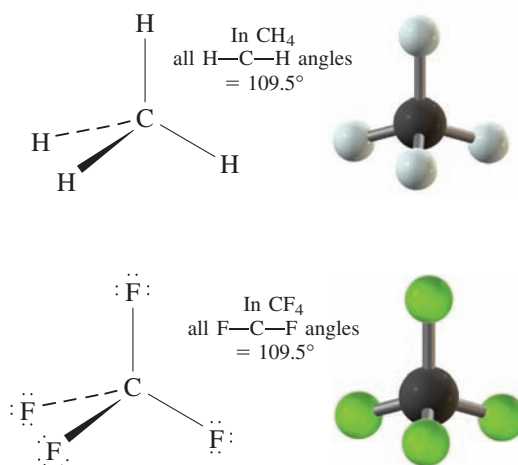


The ammonium ion, NH_4^+ , is a familiar example of a polyatomic ion of this type. In an ammonium ion, the central atom is located at the center of a regular tetrahedron with the other atoms at the corners ($H-N-H$ bond angles = 109.5°).



B. VSEPR Theory

VSEPR theory predicts that four valence shell electron groups are directed toward the corners of a regular tetrahedron. That shape gives the maximum separation for four electron groups around one atom. Thus, VSEPR theory predicts **tetrahedral electronic geometry** for an AB_4 molecule that has no unshared electrons on A. There are no lone pairs of electrons on the central atom, so a bonded atom is at each corner of the tetrahedron. VSEPR theory predicts a *tetrahedral molecular geometry* for each of these molecules.



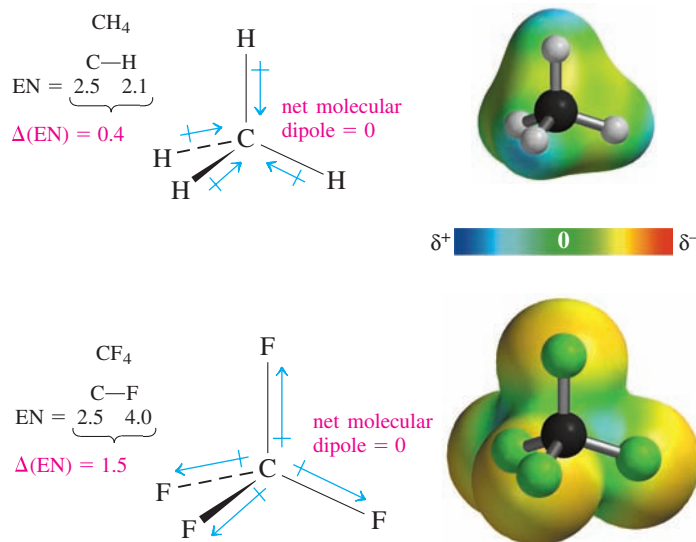
The results that we discussed in Sections 8-5 (BeX_2 , CdX_2 , and HgX_2 , where $X = Cl$, Br , or I), and 8-6 (BX_3 , where $X = F$, Cl , Br , or I), and in this section (CH_4 , CF_4 , CCl_4 , SiH_4 , SiF_4 , and NH_4^+) illustrate an important generalization:

STOP & THINK

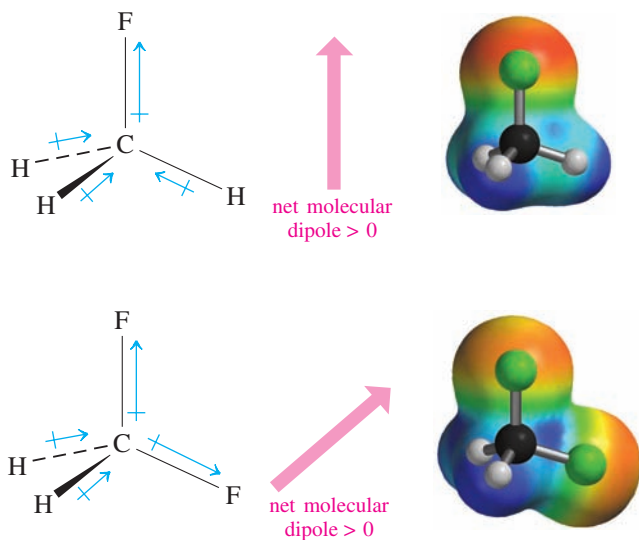
This is a good generalization to remember.

When a molecule or polyatomic ion has no lone pairs of valence electrons on the central atom, the *molecular geometry is the same as the electronic geometry*.

Examination of bond dipoles shows that in CH₄ the individual bonds are only slightly polar, whereas in CF₄ the bonds are quite polar. In CH₄ the bond dipoles are directed toward carbon, but in CF₄ they are directed away from carbon. Both molecules are very symmetrical, so the bond dipoles cancel, and both molecules are nonpolar. This is true for all AB₄ molecules in which there are *no unshared electron pairs on the central element* and all four B atoms are identical.



In some tetrahedral molecules, the atoms bonded to the central atom are not all the same. Such molecules are usually polar, with the degree of polarity depending on the relative sizes of the bond dipoles present. In CH₃F or CH₂F₂, for example, the addition of unequal dipoles makes the molecule polar.

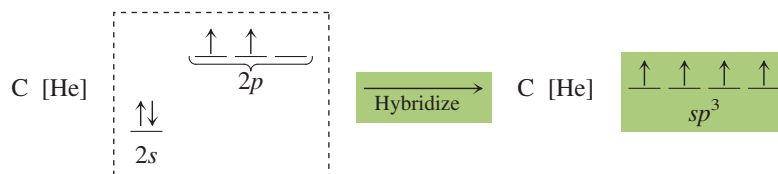


The VSEPR theory also predicts that the NH₄⁺ ion has tetrahedral electronic geometry. Each region of high electron density bonds the central atom to another atom (H in NH₄⁺) at the corner of the tetrahedral arrangement. We describe the molecular geometry of this ion as tetrahedral.

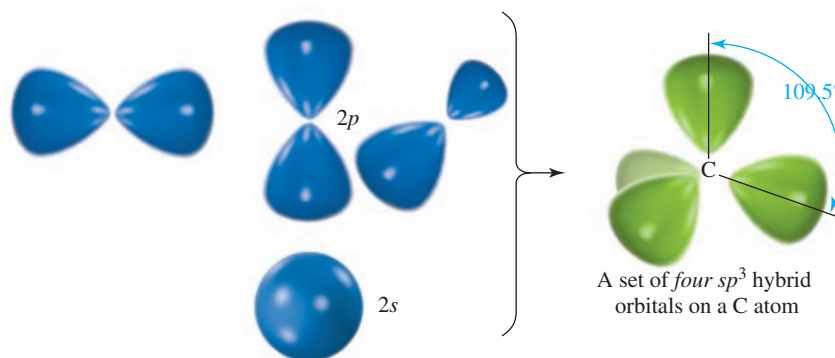
You may wonder whether square planar AB_4 molecules exist. We will discuss some examples of square planar AB_4 species in Section 8-12. The bond angles in square planar molecules are only 90° . Most AB_4 molecules are tetrahedral, however, with larger bond angles (109.5°) and greater separation of valence electron pairs around A.

C. Valence Bond Theory

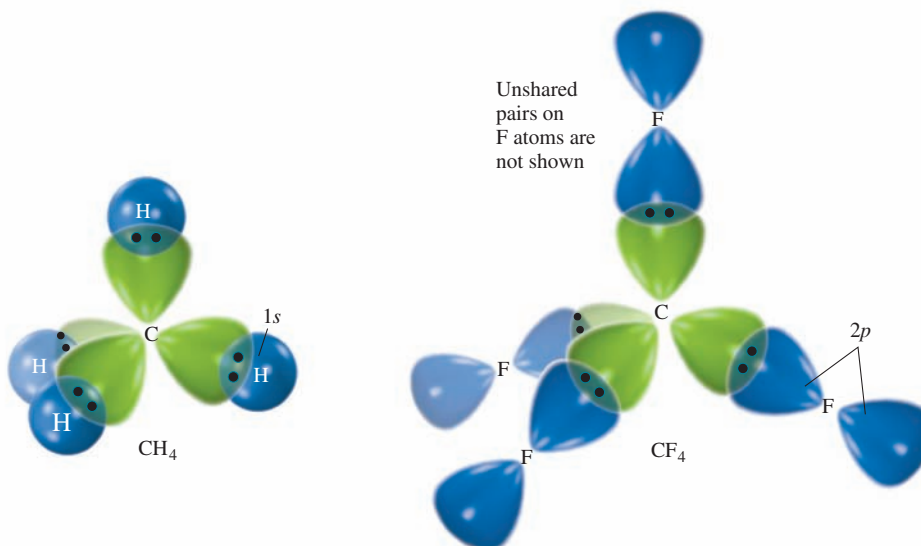
According to VB theory, each Group 4A atom (e.g., C in CH_4) must make four equivalent orbitals available for bonding. To do this, C forms four sp^3 hybrid orbitals by mixing the s and all three p orbitals in its outer ($n = 2$) shell. This results in four unpaired electrons.



These sp^3 hybrid orbitals are directed toward the corners of a regular tetrahedron, which has a 109.5° angle from any corner to the center to any other corner.



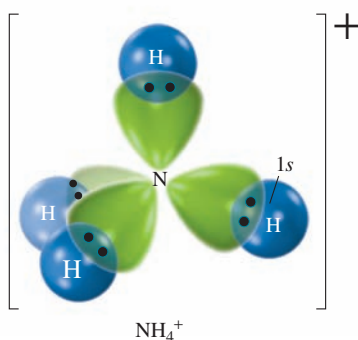
Each of the four atoms that bond to C has a half-filled atomic orbital; these can overlap the half-filled sp^3 hybrid orbitals on C, as is illustrated for CH_4 and CF_4 .



Problem-Solving Tip Use Periodic Relationships

Because F, Cl, Br, and I are all in the same group of the periodic table, we know that their compounds will be similar. We expect that the detailed descriptions we have seen for CF₄ will also apply to CCl₄, CBr₄, and CI₄, and we do not need to go through the entire reasoning for each one. Thus, we can say that each of the CX₄ molecules (X = F, Cl, Br, or I) also has tetrahedral electronic geometry, tetrahedral molecular geometry, *sp*³ hybridization on the carbon atom, zero dipole moment, and so on.

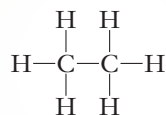
We can give the same VB description for the hybridization of the central atoms in polyatomic ions. In NH₄⁺ the N atom forms four *sp*³ hybrid orbitals directed toward the corners of a regular tetrahedron. Each of these *sp*³ hybrid orbitals overlaps with an orbital on a neighboring atom (H in NH₄⁺) to form a bond.



When there are four electron groups around the central atom, it is *sp*³ hybridized. AB₄ molecules and ions with no lone pairs on the central atom have tetrahedral electronic geometry, tetrahedral molecular geometry, and *sp*³ hybridization on the central atom.

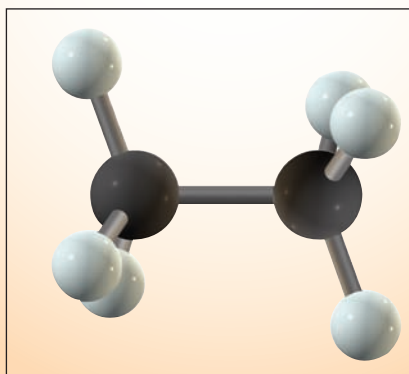
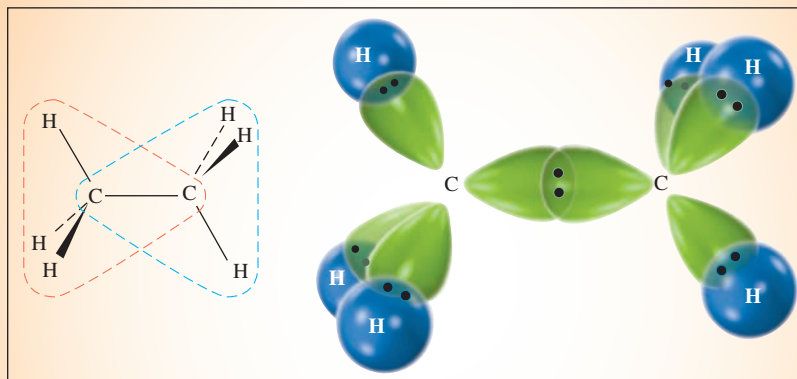
Problem-Solving Tip Often There Is More Than One Central Atom

Many molecules contain more than one central atom, that is, there is more than one atom that is bonded to several other atoms. We can analyze such molecules one central atom at a time, to build up a picture of the three-dimensional aspects of the molecule. An example is ethane, C₂H₆; its Lewis formula is



Let us first consider the left-hand carbon atom. The arrangement of its electron groups allows us to locate the other C and three H atoms with respect to that C atom (the atoms outlined in red below). Then we carry out a similar analysis for the right-hand C atom to deduce the arrangements of its neighbors (outlined in blue).

Each C atom in C_2H_6 has four electron groups. The VSEPR theory tells us that each C atom has tetrahedral electronic geometry; the resulting atomic arrangement around each C atom has one C and three H atoms at the corners of this tetrahedral arrangement. The VB interpretation is that each C atom is sp^3 hybridized. The C—C bond is formed by overlap of a half-filled sp^3 hybrid orbital of one C atom with a half-filled sp^3 hybrid orbital of the other C atom. Each C—H bond is formed by the overlap of a half-filled sp^3 hybrid orbital on C with the half-filled $1s$ orbital of an H atom.



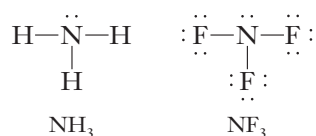
8-8 Tetrahedral Electronic Geometry: AB_3U Species (One Lone Pair on A)

We are now ready to study the structures of some simple molecules with lone pairs on the central atom. In this and subsequent sections, we use generalized chemical formulas in which “A” represents the central atom, “B” represents an atom bonded to A, and “U” represents a lone (unshared) pair on the central atom A. For instance, AB_3U would represent any molecule with three B atoms bonded to a central atom A, with one lone pair on A.

A. Experimental Facts and Lewis Formulas

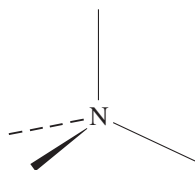
Each Group 5A element has five electrons in its valence shell. The Group 5A elements form some covalent compounds by sharing three of those electrons with three other atoms. Let us describe two examples: ammonia, NH_3 , and nitrogen trifluoride, NF_3 . Each is a trigonal pyramidal, polar molecule with a lone pair on the nitrogen atom. Each has a nitrogen atom at the apex and the other three atoms at the corners of the triangular base of the pyramid.

The Lewis formulas for NH₃ and NF₃ are

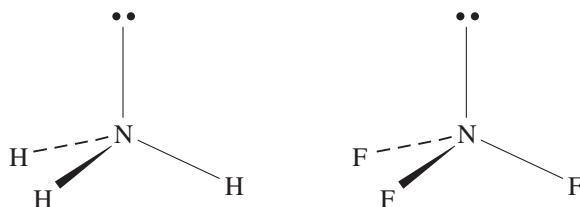


B. VSEPR Theory

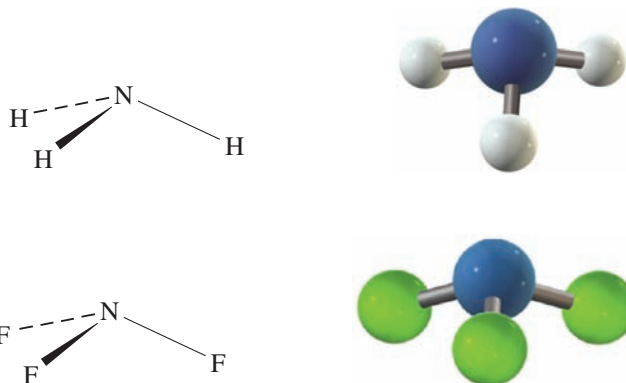
As in Section 8-7, VSEPR theory predicts that the *four* electron groups around a central atom will be directed toward the corners of a tetrahedron because this gives maximum separation. So N has tetrahedral electronic geometry in NH₃ and NF₃. We must reemphasize the distinction between electronic geometry and molecular geometry. *Electronic geometry* refers to the geometric arrangement of the *electron groups* around the central atom. But the *molecular geometry* excludes the lone pairs on the central atom, and describes only the arrangement of *atoms* (i.e., nuclei) around the central atom. We can represent the tetrahedral *electronic geometry* around N in NH₃ or NF₃ as follows.



We then use the Lewis formula as a guide to arrange the bonded atoms and the lone pairs in these tetrahedral sites around the nitrogen atom to give the molecular geometry.



Then we describe the *molecular geometry* as the arrangement of the *atoms*. In each of these molecules, the N atom is at the apex of a (shallow) trigonal pyramidal arrangement and the other three atoms are at the corners of the triangular base of the pyramid. Thus, the molecular geometry of each molecule is described as **trigonal pyramidal**.

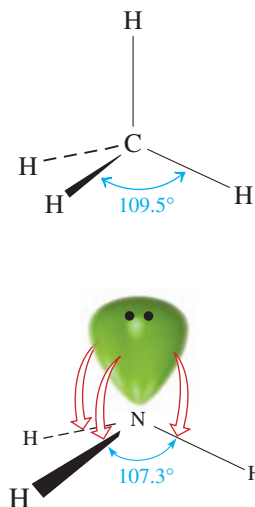


STOP & THINK

When there are lone pairs on the central atom the molecular geometry is *not* the same as the electronic geometry, because lone pairs must occupy space of their own.

We have seen that CH_4 , CF_4 , NH_3 , and NF_3 all have tetrahedral electronic geometry. But CH_4 and CF_4 (AB_4) have tetrahedral molecular geometry, whereas NH_3 and NF_3 (AB_3U) have trigonal pyramidal molecular geometry.

In molecules or polyatomic ions that contain lone (unshared) pairs of valence electrons on the central atom, the *electronic geometry* and the *molecular geometry* cannot be the same.

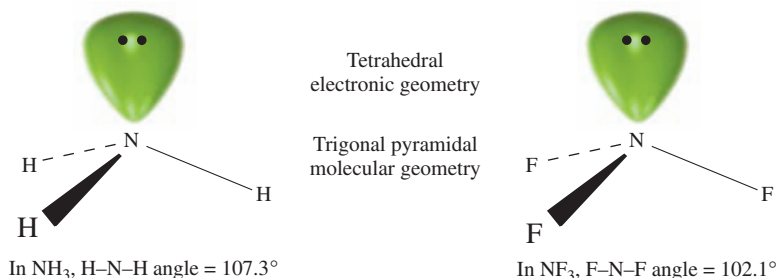
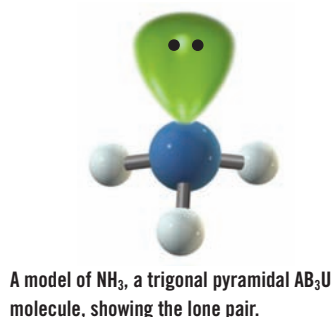


Because this trigonal pyramidal molecular geometry is a fragment of tetrahedral electronic geometry, we expect that the $\text{H}-\text{N}-\text{H}$ angle would be close to the tetrahedral value, 109.5° . In CH_4 (a tetrahedral AB_4 molecule), all $\text{H}-\text{C}-\text{H}$ bond angles are observed to be this ideal value, 109.5° . In NH_3 , however, the $\text{H}-\text{N}-\text{H}$ bond angles are observed to be less than this, 107.3° . How can we explain this deviation?

A lone pair is a pair of valence electrons that is associated with only one nucleus in contrast to a bonded pair, which is associated with two nuclei. The known geometries of many molecules and polyatomic ions, based on measurements of bond angles, show that *lone pairs of electrons occupy more space than bonding pairs*. A lone pair has only one atom exerting strong attractive forces on it, so it can spread out and take up more space than bonding electrons. The relative magnitudes of the repulsive forces between pairs of electrons on an atom are

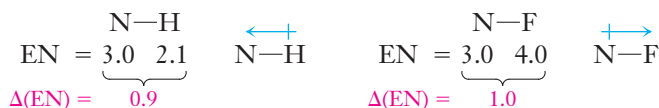
$$lp/lp \gg lp/bp > bp/bp$$

where lp refers to lone pairs and bp refers to bonding pairs of electrons. We are most concerned with the repulsions among the electrons in the valence shell of the *central atom* of a molecule or polyatomic ion. The angles at which repulsive forces among electron pairs are minimized are the angles at which the bonding pairs and lone pairs are found in covalently bonded molecules and polyatomic ions. Due to lp/bp repulsions in NH_3 and NF_3 , their bond angles are *less* than the angles of 109.5° we observed in CH_4 and CF_4 molecules.

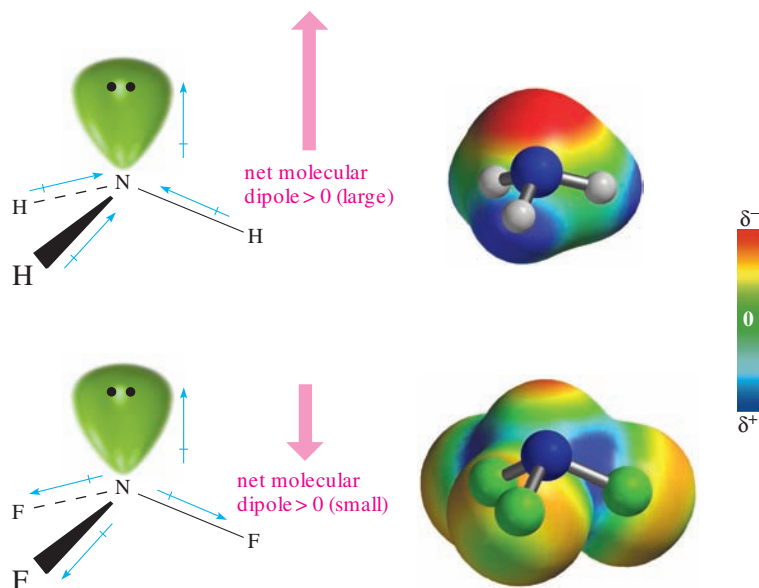


The formulas are frequently written as $:\text{NH}_3$ and $:\text{NF}_3$ to emphasize the lone pairs of electrons. The lone pairs must be considered when the polarities of these molecules are examined; they are extremely important in chemical reactions. This is why NH_3 is a base, as we saw in Section 6-1.4 and as we shall discuss more fully in Chapter 10. The contribution of each lone pair to polarity can be depicted as shown below and discussed in the margin.

The electronegativity differences in NH_3 and NF_3 are nearly equal, *but* the resulting nearly equal bond polarities are in opposite directions.



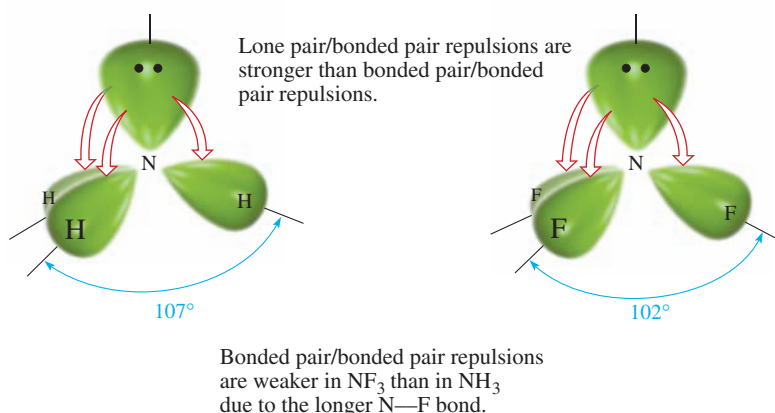
Thus, we have



► In NH_3 the bond dipoles *reinforce* the effect of the lone pair, so NH_3 is very polar ($\mu = 1.47 \text{ D}$).

► In NF_3 the bond dipoles *oppose* the effect of the unshared pair, so NF_3 is only slightly polar ($\mu = 0.23 \text{ D}$).

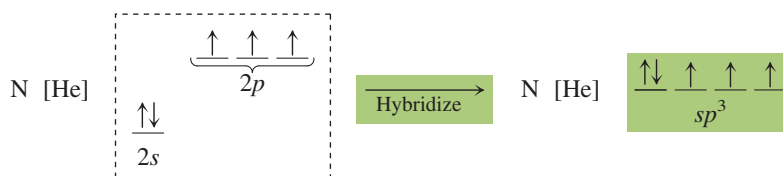
We can now use this information to explain the bond angles observed in NF_3 and NH_3 . Because of the direction of the bond dipoles in NH_3 , the electron-rich end of each $\text{N}-\text{H}$ bond is at the central atom, N. On the other hand, the fluorine end of each bond in NF_3 is the electron-rich end. As a result, the lone pair can more closely approach the N in NF_3 than in NH_3 . In NF_3 the lone pair therefore exerts greater repulsion toward the bonded pairs than in NH_3 . In addition, the longer $\text{N}-\text{F}$ bond length makes the $bp-bp$ distance greater in NF_3 than in NH_3 , so that the bp/bp repulsion in NF_3 is less than that in NH_3 . The net effect is that the bond angles are reduced more in NF_3 . We can represent this situation as:



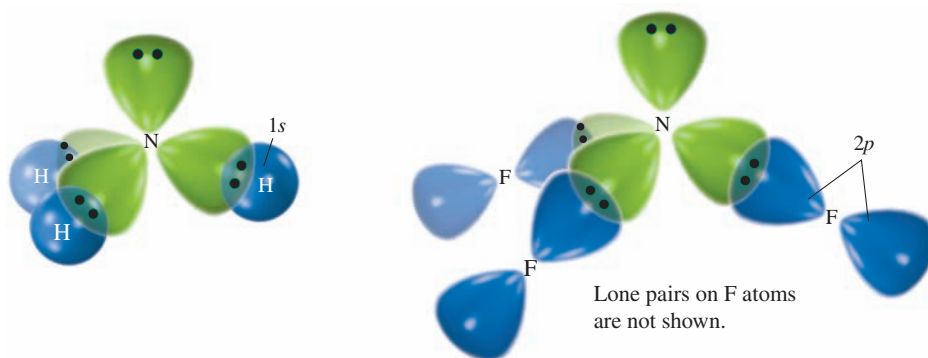
► We might expect the larger F atoms ($r = 0.75 \text{ \AA}$) to repel each other more strongly than the H atoms ($r = 0.37 \text{ \AA}$), leading to larger bond angles in NF_3 than in NH_3 . This is not the case, however, because the $\text{N}-\text{F}$ bond is longer than the $\text{N}-\text{H}$ bond. The $\text{N}-\text{F}$ bond density is farther from the N than the $\text{N}-\text{H}$ bond density.

C. Valence Bond Theory

Experimental results suggest four nearly equivalent orbitals (three involved in bonding, a fourth to accommodate the lone pair), so we again need four sp^3 hybrid orbitals.



In both NH_3 and NF_3 , the lone pair of electrons occupies one of the sp^3 hybrid orbitals. Each of the other three sp^3 orbitals participates in bonding by sharing electrons with another atom. They overlap with half-filled H $1s$ orbitals and F $2p$ orbitals in NH_3 and NF_3 , respectively.



AB_3U molecules and ions, each having four electron groups around the central atom, *usually* have tetrahedral electronic geometry, trigonal pyramidal molecular geometry, and sp^3 hybridization on the central atom.

We must remember that *theory* (and its application) depends on fact, not the other way around. Sometimes the experimental facts are not consistent with the existence of hybrid orbitals. In PH_3 and AsH_3 , each $\text{H}-\text{P}-\text{H}$ bond angle is 93.7° , and each $\text{H}-\text{As}-\text{H}$ bond angle is 91.8° . These angles very nearly correspond to three p orbitals at 90° to each other. Thus, there appears to be no need to use the VSEPR theory or hybridization to describe the bonding in these molecules. In such cases, we just use the “pure” atomic orbitals rather than hybrid orbitals to describe the bonding.

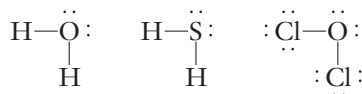
Problem-Solving Tip When Do We Not Need to Describe Hybrid Orbitals?

Students often wonder how to recognize when hybridization does not apply, as in the PH_3 and AsH_3 cases just described and in H_2S (see Section 8-9). Remember that models such as hybridization are our attempts to explain observations such as bond angles. At the level of our studies, we will be given information about the observed molecular geometry, such as measured bond angles. If these are near the angles of pure (unhybridized) orbitals, then hybridization is not needed; if they are near the predicted angles for hybridized orbitals, then hybridization should be used. If no information about observed molecular geometry (molecular shape, bond angles, etc.) is supplied, you should assume that the VSEPR and hybridization approaches presented in this chapter should be used.

8-9 Tetrahedral Electronic Geometry: AB_2U_2 Species (Two Lone Pairs on A)

A. Experimental Facts and Lewis Formulas

Each Group 6A element has six electrons in its valence shell. The Group 6A elements form many covalent compounds by sharing a pair of electrons with each of two other atoms. Typical examples are H_2O , H_2S , and Cl_2O . The Lewis formulas for these molecules are

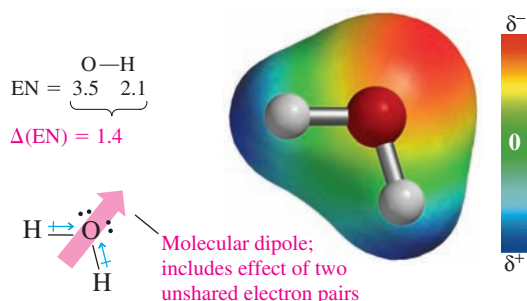


All are angular, polar molecules. The bond angle in water, for example, is 104.5° , and the molecule is very polar with a dipole moment of 1.85 D.

B. VSEPR Theory

The VSEPR theory predicts that the four electron pairs around the oxygen atom in H₂O should be 109.5° apart in a tetrahedral arrangement. The observed H—O—H bond angle is 104.5° . The two lone pairs strongly repel each other and the bonding pairs of electrons. These repulsions force the bonding pairs closer together and result in the decreased bond angle. The decrease in the H—O—H bond angle (from 109.5° to 104.5°) is greater than the corresponding decrease in the H—N—H bond angles in ammonia (from 109.5° to 107.3°) because of the stronger *lp/lp* repulsion in H₂O.

The electronegativity difference is large (1.4 units), so each O—H bond is quite polar. Additionally, the bond dipoles *reinforce* the effect of the two lone pairs, so the H₂O molecule is very polar. Its dipole moment is 1.8 D. The unusual properties of water can be explained in large part by its high polarity.

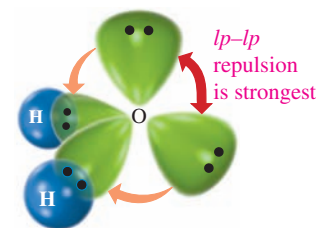
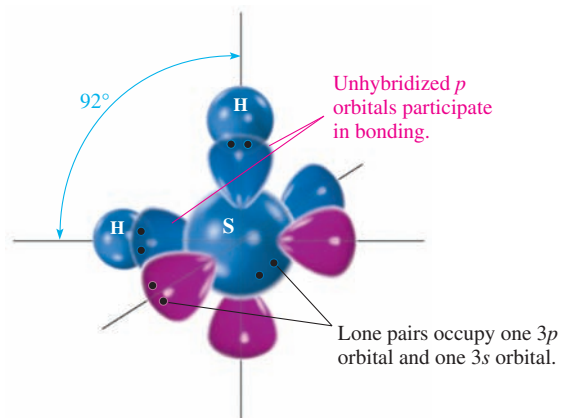


C. Valence Bond Theory

The bond angle in H₂O (104.5°) is closer to the tetrahedral value (109.5°) than to the 90° angle that would result from bonding by pure *2p* atomic orbitals on O. Valence bond theory therefore postulates four *sp*³ hybrid orbitals centered on the O atom: two that participate in bonding and two that hold the two lone pairs.

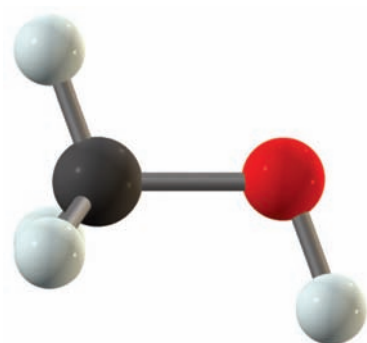
AB₂U₂ molecules and ions, each having four electron groups around the central atom, *usually* have tetrahedral electronic geometry, angular molecular geometry, and *sp*³ hybridization on the central atom.

Hydrogen sulfide, H₂S, is also an angular molecule, but the H—S—H bond angle is 92.2° . This is very close to the 90° angles between two unhybridized *3p* orbitals of S. We therefore *do not* need to propose hybrid orbitals to describe the bonding in H₂S. The two H atoms are able to exist at approximately right angles to each other when they are bonded to the larger S atom. The bond angles in H₂Se and H₂Te are 91° and 89.5° , respectively, indicating that they also use pure *p* orbitals for bonding.



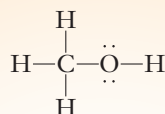
There are now *two* lone pairs that repel the bonded pairs.

► Sulfur is in Group 6A, directly below oxygen.

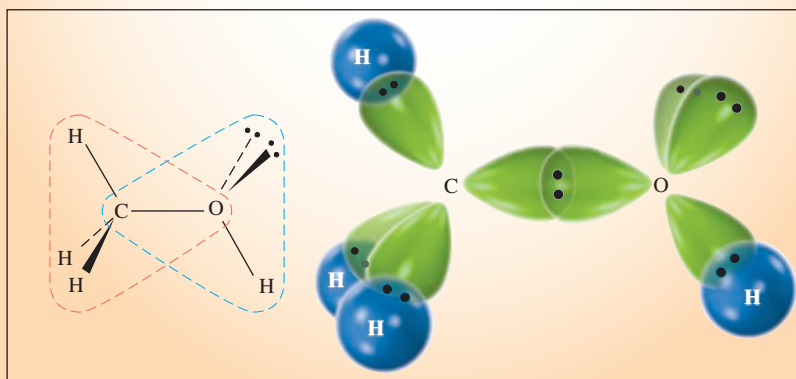


Problem-Solving Tip Some Molecules Have Two Central Atoms and Lone Pairs

Methanol, CH_3OH , is a simple molecule that has more than one central atom *and* two lone pairs. It is the simplest member of a family of organic molecules called *alcohols*; all alcohols contain the atom grouping $\text{C} - \text{O} - \text{H}$. The Lewis formula for methanol is

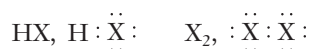


Again, we consider the arrangements around two central atoms in sequence. The carbon atom has four electron groups (outlined below in red). VSEPR theory tells us that this atom has tetrahedral *electronic* geometry; the resulting atomic arrangement around the C atom has four atoms (O and three H) at the corners of this tetrahedral arrangement, so the molecular geometry about the C atom is tetrahedral. The oxygen atom has four electron groups (outlined in blue), so it, too, has tetrahedral *electronic* geometry. Thus, the $\text{C} - \text{O} - \text{H}$ arrangement is angular, and there are two lone pairs on O. The VB interpretation is that both atoms are sp^3 hybridized. The $\text{C} - \text{O}$ bond is formed by overlap of a half-filled sp^3 hybrid orbital on the C atom with a half-filled sp^3 hybrid orbital on the O atom. Each covalent bond to an H is formed by the overlap of a half-filled sp^3 hybrid orbital with the half-filled $1s$ orbital on an H atom. Each lone pair of electrons on O is in an sp^3 hybrid orbital.



8-10 Tetrahedral Electronic Geometry: ABU_3 Species (Three Lone Pairs on A)

► We represent the halogen as X.



In the latter case, either halogen may be considered the A atom of AB.

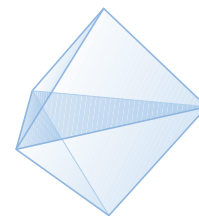
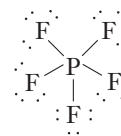
Each Group 7A element has seven electrons in its highest occupied energy level. The Group 7A elements form molecules such as $\text{H} - \text{F}$, $\text{H} - \text{Cl}$, $\text{Cl} - \text{Cl}$, and $\text{I} - \text{I}$ by sharing one of their electrons with another atom. The other atom contributes one electron to the bonding. Lewis formulas for these molecules are shown in the margin. Any diatomic molecule must be linear. Neither VSEPR theory nor VB theory adds anything to what we already know about the molecular geometry of such molecules.

8-11 Trigonal Bipyramidal Electronic Geometry: AB_5 , AB_4U , AB_3U_2 , and AB_2U_3

A. Experimental Facts and Lewis Formulas

In Section 8-8 we saw that the Group 5A elements form some molecules by sharing only three of their five electrons with other atoms (e.g., NH_3 , NF_3 , and PCl_3). Group 5A

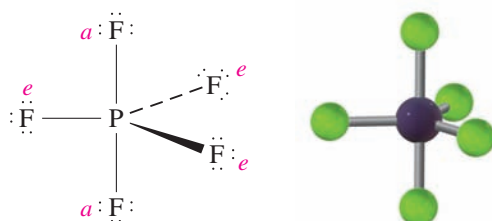
elements (P, As, and Sb) beyond the second period also form some covalent compounds by sharing all five of their valence electrons with five other atoms (see Section 7-8). Phosphorus pentafluoride, PF₅ (mp = -83°C), is such a compound. Each P atom has five valence electrons to share with five F atoms. The Lewis formula for PF₅ (see Example 7-6) is shown in the margin. PF₅ molecules are **trigonal bipyramidal** nonpolar molecules. A **trigonal bipyramid** is a six-sided polyhedron consisting of two pyramids joined at a common triangular (trigonal) base.



► A trigonal bipyramid.

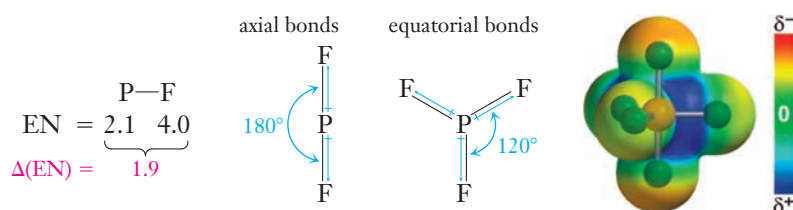
B. VSEPR Theory

The VSEPR theory predicts that the five electron groups around the phosphorus atom in PF₅ should be as far apart as possible. Maximum separation of five electron groups around a central atom is achieved when the five electron groups (bonding pairs) are placed at the corners and the central atom (P) is placed in the center of a trigonal (or triangular) bipyramid. This is in agreement with experimental observation.



The three F atoms marked *e* are at the corners of the common base, in the same plane as the P atom. These are called *equatorial* F atoms (*e*). The other two F atoms, one above and one below the plane, are called *axial* F atoms (*a*). The F—P—F bond angles are 90° (axial to equatorial), 120° (equatorial to equatorial), and 180° (axial to axial).

The large electronegativity difference between P and F (1.9) suggests very polar bonds. Let's consider the bond dipoles in two groups, because there are two different kinds of P—F bonds in PF₅ molecules, axial and equatorial.



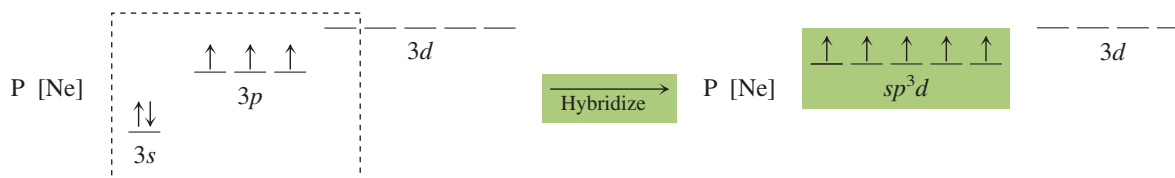
► Are there other ways that five fluorine atoms could be arranged *symmetrically* around a phosphorus atom? Compare the hypothetical bond angles in such arrangements with those in a trigonal bipyramidal arrangement.

► The two axial bonds are in a linear arrangement, like the two bonds in BeCl₂ (see Section 8-5); the three equatorial bonds are in a trigonal planar arrangement, like the three bonds in BF₃ (see Section 8-6).

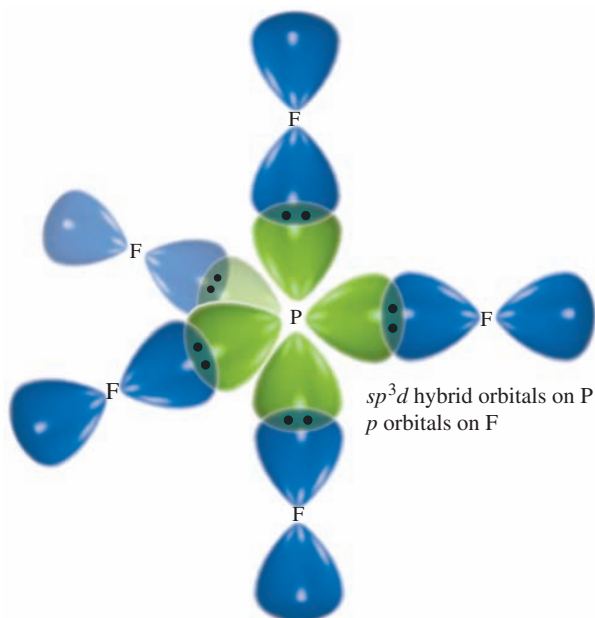
The two axial bond dipoles cancel each other, and the three equatorial bond dipoles cancel, so PF₅ molecules are nonpolar.

C. Valence Bond Theory

Because phosphorus is the central atom in a PF₅ molecule, it must have available five orbitals to form bonds with five F atoms. Hybridization involves one *d* orbital from the vacant set of 3*d* orbitals along with the 3*s* and 3*p* orbitals of the P atom.



The five sp^3d hybrid orbitals on P point toward the corners of a trigonal bipyramid. Each of these half-filled orbitals is overlapped by a singly occupied $2p$ orbital of an F atom. The resulting pairing of P and F electrons forms five covalent bonds.



When there are five electron groups around the central atom, it is sp^3d hybridized. AB_5 molecules and ions with no lone pairs on the central atom have trigonal bipyramidal electronic geometry, trigonal bipyramidal molecular geometry, and sp^3d hybridization on the central atom.

► The P atom is said to have an *expanded valence shell* (see Section 7-8).

We see that sp^3d hybridization uses an available d orbital in the outermost occupied shell of the central atom. The heavier Group 5A elements—P, As, and Sb—can form five covalent bonds using this hybridization. But nitrogen, also in Group 5A, cannot form five covalent bonds because the valence shell of N has no d orbitals (only one s and three p orbitals). The set of s and p orbitals in a given energy level (and therefore any set of hybrids composed only of s and p orbitals) can accommodate a *maximum* of eight electrons and participate in a *maximum* of four covalent bonds. The same is true of all elements of the second period because they have only s and p orbitals in their valence shells. No atoms in the first and second periods can exhibit expanded valence.

D. Lone Pairs in Trigonal Bipyramidal Electronic Geometry

► Reminder: The relative magnitudes of repulsive forces are:

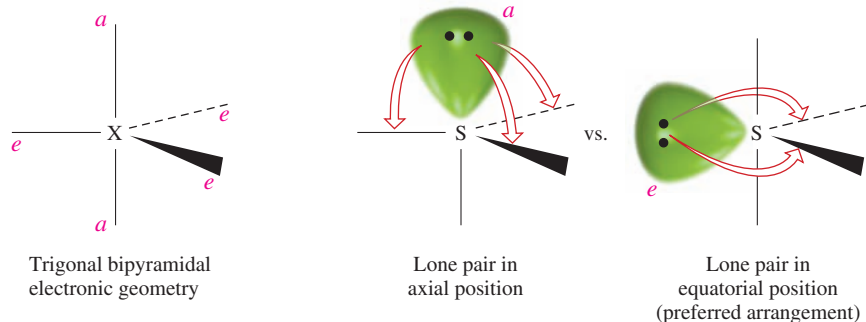
$$lp/lp \gg lp/bp > bp/bp$$

As we saw in Parts B of Sections 8-8 and 8-9, lone pairs of electrons occupy more space than bonding pairs, resulting in increased repulsions from lone pairs. What happens when one or more of the five electron groups on the central atom are lone pairs? Let us first consider a molecule such as SF_4 , for which the Lewis formula is

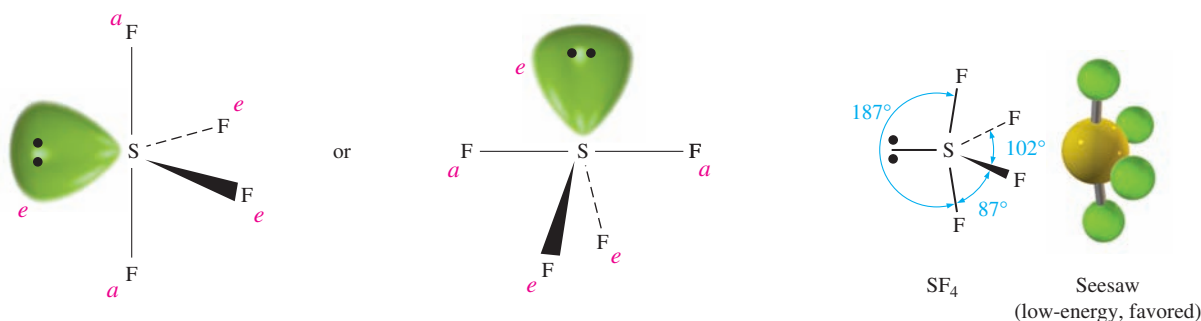


The central atom, S, is bonded to four atoms and has one lone pair. This is an example of the general formula AB_4U . Sulfur has five electron groups, so we know that the electronic geometry is trigonal bipyramidal and the bonding orbitals are sp^3d hybrids. But now a new question arises: Is the arrangement more stable with the lone pair in an axial (*a*) or in an equatorial (*e*) position? If it were in an axial position, it would be 90° from the *three* closest

other pairs (the pairs bonding three F atoms in equatorial positions) and 180° from the other axial pair. If it were in an equatorial position, only the *two* axial pairs would be at 90° from the lone pair, and the two equatorial pairs would be farther away, at 120°. The lone pair would therefore be less crowded in an *equatorial* position.

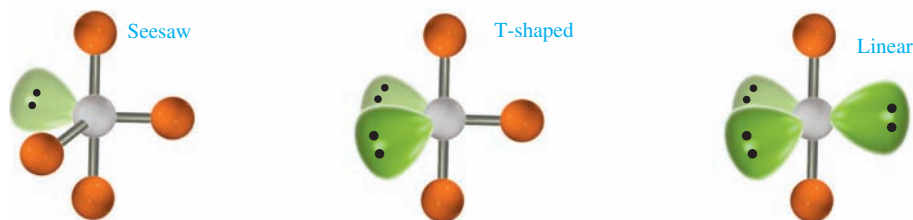
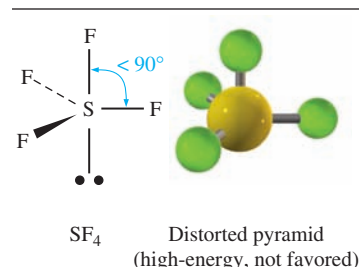


The four F atoms then occupy the remaining four positions. We describe the resulting arrangement of *atoms* as a **seesaw arrangement**. Imagine rotating the arrangement so that the line joining the two axial positions is the board on which the two seesaw riders sit, and the two bonded equatorial positions are the pivot of the seesaw.



As we saw in Sections 8-8 and 8-9, the differing magnitudes of repulsions involving lone pairs and bonding pairs often result in observed bond angles that are slightly different from idealized values. For instance, *lp/bp* repulsion in the seesaw molecule SF₄ causes distortion of the axial S—F bonds away from the lone pair, to an angle of 177°; the two equatorial S—F bonds, ideally at 120°, move much closer together to an angle of 101.6°.

By the same reasoning, we understand why additional lone pairs also take equatorial positions (AB₃U₂ with both lone pairs equatorial or AB₂U₃ with all three lone pairs equatorial). These arrangements are summarized in Figure 8-2.



AB₄U 4 bonded atoms (B)
1 lone pair (U) in
equatorial position

Seesaw molecular geometry
Example: SF₄

AB₃U₂ 3 bonded atoms (B)
2 lone pairs (U) in
equatorial positions

T-shaped molecular geometry
Examples: ClF₃, BrF₃

AB₂U₃ 2 bonded atoms (B)
3 lone pairs (U) in
equatorial positions

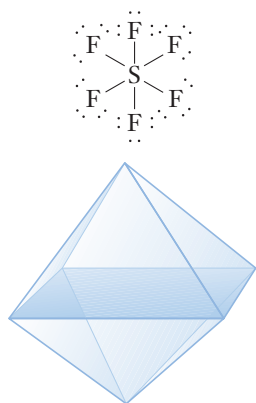
Linear molecular geometry
Examples: XeF₂, I₃[−]

Figure 8-2 Arrangements of bonded atoms and lone pairs (five electron groups—trigonal pyramidal electronic geometry).

8-12 Octahedral Electronic Geometry: AB_6 , AB_5U , and AB_4U_2

A. Experimental Facts and Lewis Formulas

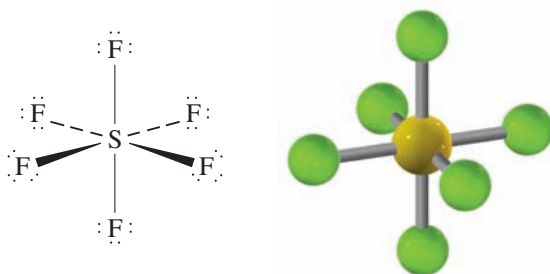
The Group 6A elements below oxygen form some covalent compounds of the AB_6 type by sharing their six valence electrons with six other atoms. Sulfur hexafluoride, SF_6 (mp = -51°C), an unreactive gas, is an example. Sulfur hexafluoride molecules are nonpolar octahedral molecules. The hexafluorophosphate ion, PF_6^- , is an example of a polyatomic ion of the type AB_6 .



► In a *regular octahedron*, each of the eight faces is an equilateral triangle.

B. VSEPR Theory

An SF_6 molecule has six valence shell electron pairs and six F atoms surrounding one S atom. Because the valence shell of sulfur contains no lone pairs, the electronic and molecular geometries in SF_6 are identical. The maximum separation possible for six electron groups around one S atom is achieved when the electron groups are at the corners and the S atom is at the center of a regular octahedron. Thus, VSEPR theory is consistent with the observation that SF_6 molecules are **octahedral**.

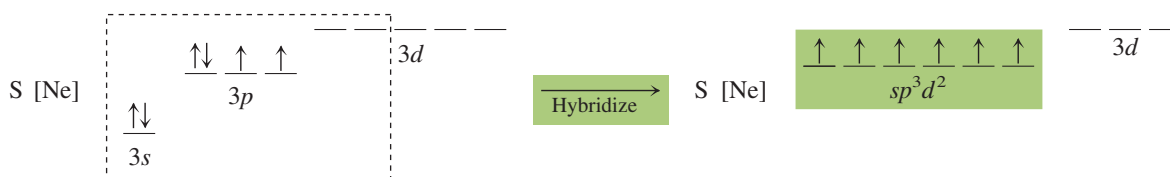


In this octahedral molecule the $F-S-F$ bond angles are 90° and 180° . Each $S-F$ bond is quite polar, but each bond dipole is canceled by an equal dipole 180° from it. So the large bond dipoles cancel and the SF_6 molecule is nonpolar.

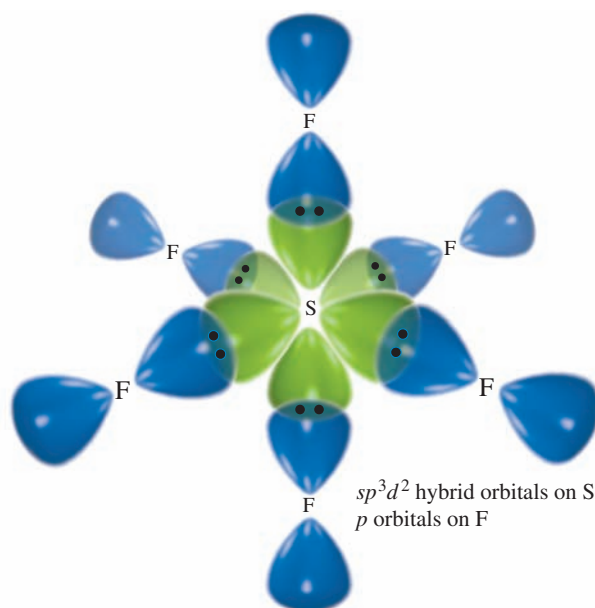
By similar reasoning, VSEPR theory predicts octahedral electronic geometry and octahedral molecular geometry for the PF_6^- ion, which has six valence shell electron pairs and six F atoms surrounding one P atom.

C. Valence Bond Theory

Sulfur atoms can use one $3s$, three $3p$, and two $3d$ orbitals to form six hybrid orbitals that accommodate six electron pairs:



The six **sp^3d^2 hybrid orbitals** are directed toward the corners of a regular octahedron. Each sp^3d^2 hybrid orbital is overlapped by a half-filled $2p$ orbital from fluorine to form a total of six covalent bonds.



► Se and Te, in the same group, form analogous compounds. O cannot do so, because it does not have low-energy d orbitals available with which the s and p orbitals can hybridize.

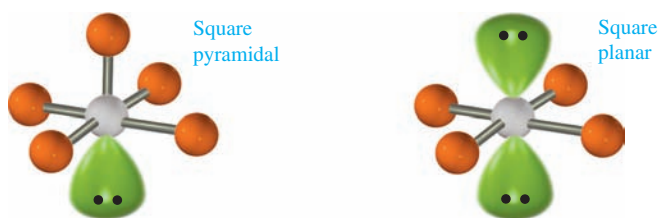
An analogous picture could be drawn for the PF_6^- ion.

When there are six electron groups around the central atom, it is sp^3d^2 hybridized. AB_6 molecules and ions with no lone pairs on the central atom have octahedral electronic geometry, octahedral molecular geometry, and sp^3d^2 hybridization on the central atom.

D. Lone Pairs in Octahedral Electronic Geometry

We can reason along the lines used in Part D of Section 8-11 to predict the preferred locations of lone pairs on the central atom in octahedral electronic geometry. Because of the high symmetry of the octahedral arrangement, all six positions are equivalent, so it does not matter in which position in the drawing we put the first lone pair. AB_5U molecules and ions are described as having **square pyramidal** molecular geometry. When a second lone pair is present, the most stable arrangement has the two lone pairs in two octahedral positions at 180° angles from each other. This leads to a **square planar** molecular geometry for AB_4U_2 species. These arrangements are shown in Figure 8-3.

► Two lone pairs at 90° from each other would be much more crowded.



AB_5U 5 bonded atoms (B)
 1 lone pair (U)

Square pyramidal molecular geometry
Examples: IF_5 , BrF_5

AB_4U_2 4 bonded atoms (B)
 2 lone pairs (U)

Square planar molecular geometry
Examples: XeF_4 , IF_4^-

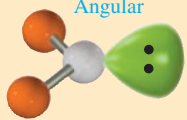
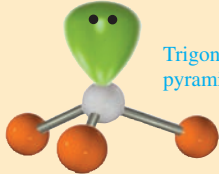
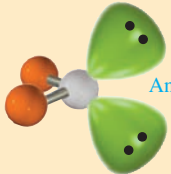
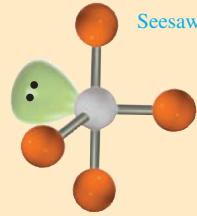
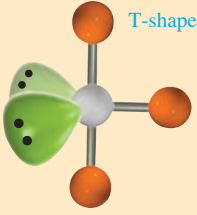
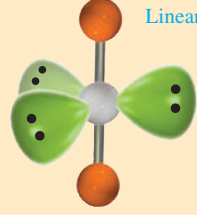
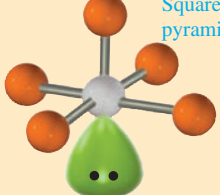
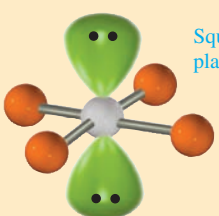
Figure 8-3 Arrangements of bonded atoms and lone pairs (six electron groups—octahedral electronic geometry).

8-13 Lone Pairs on the Central Atom—A Summary

Table 8-3 summarizes a great deal of information about molecules and ions with lone pairs on the central atom. You should study this table carefully.

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 8-3 Molecular Geometry of Species with Lone Pairs (U) on the Central Atom

General Formula	Electron Groups ^a	Electronic Geometry	Hybridization at Central Atom	Lone Pairs	Molecular Geometry	Examples
AB ₂ U	3	trigonal planar	sp^2	1	Angular 	O ₃ , NO ₂ ⁻ , SO ₂
AB ₃ U	4	tetrahedral	sp^3	1	Trigonal pyramidal 	NH ₃ , SO ₃ ²⁻
AB ₂ U ₂	4	tetrahedral	sp^3	2	Angular 	H ₂ O, NH ₂ ⁻
AB ₄ U	5	trigonal bipyramidal	sp^3d	1	Seesaw 	SF ₄
AB ₃ U ₂	5	trigonal bipyramidal	sp^3d	2	T-shaped 	ICl ₃ , ClF ₃
AB ₂ U ₃	5	trigonal bipyramidal	sp^3d	3	Linear 	XeF ₂ , I ₃ ⁻
AB ₅ U	6	octahedral	sp^3d^2	1	Square pyramidal 	IF ₅ , BrF ₅
AB ₄ U ₂	6	octahedral	sp^3d^2	2	Square planar 	XeF ₄ , IF ₄ ⁻

^aRemember that double and triple bonds are treated as one electron group for determining VSEPR geometries.

Unless otherwise noted, all content on this page is © Cengage Learning.

Problem-Solving Tip Placing Lone Pairs on the Central Atom

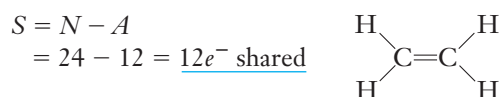
Remember that lone pairs occupy more space than bonded pairs, so the lone pairs are always put in positions where they will be least crowded.

If the Lewis formula for a molecule or ion shows only one lone pair: In linear, trigonal planar, tetrahedral, or octahedral electronic geometry, all positions are equivalent, so it doesn't matter where we place the lone pair. In trigonal bipyramidal electronic geometry, place the lone pair in the equatorial position where it is least crowded, and put the bonded atoms in the other positions.

If the Lewis formula shows two lone pairs: In trigonal planar or tetrahedral electronic geometry, we can place the lone pairs in any two positions and the bonded atoms in the other position(s). In trigonal bipyramidal electronic geometry, place the two lone pairs in two equatorial positions (120° apart) where they are least crowded, and put the bonded atoms in the other positions. In octahedral electronic geometry, place the two lone pairs in two positions *across* (180°) from each other, and put the bonded atoms in the other positions (square planar molecular geometry).

8-14 Compounds Containing Double Bonds

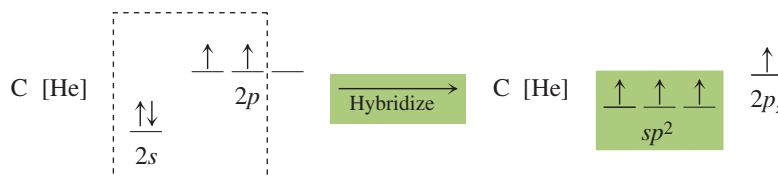
In Chapter 7 we constructed Lewis formulas for some molecules and polyatomic ions that contain double and triple bonds. We have not yet considered bonding and shapes for such species. Let us consider ethylene (ethene), C_2H_4 , as a specific example. Its Lewis formula is



Each atom has three electron groups. The VSEPR theory tells us that each C atom is at the center of a trigonal plane.

Valence bond theory describes each doubly bonded carbon atom as sp^2 hybridized, with one electron in each sp^2 hybrid orbital and one electron in the unhybridized $2p$ orbital. This $2p$ orbital is perpendicular to the plane of the three sp^2 hybrid orbitals:

► Here each C atom is considered a central atom. Remember that each bonded atom counts as *one* electron group.



Recall that sp^2 hybrid orbitals are directed toward the corners of an equilateral triangle. Figure 8-4 shows top and side views of these hybrid orbitals.

The two C atoms interact by head-on (end-to-end) overlap of sp^2 hybrids pointing toward each other to form a *sigma* (σ) bond and by side-on overlap of the unhybridized $2p$ orbitals to form a *pi* (π) bond.

A sigma bond is a bond resulting from head-on overlap of atomic orbitals. *The region of electron sharing is along and cylindrically around an imaginary line connecting the bonded atoms.*

All single bonds are sigma bonds. Many kinds of pure atomic orbitals and hybridized orbitals can be involved in sigma bond formation.

A pi bond is a bond resulting from side-on overlap of atomic orbitals. *The regions of electron sharing are on opposite sides of an imaginary line connecting the bonded atoms and parallel to this line.*

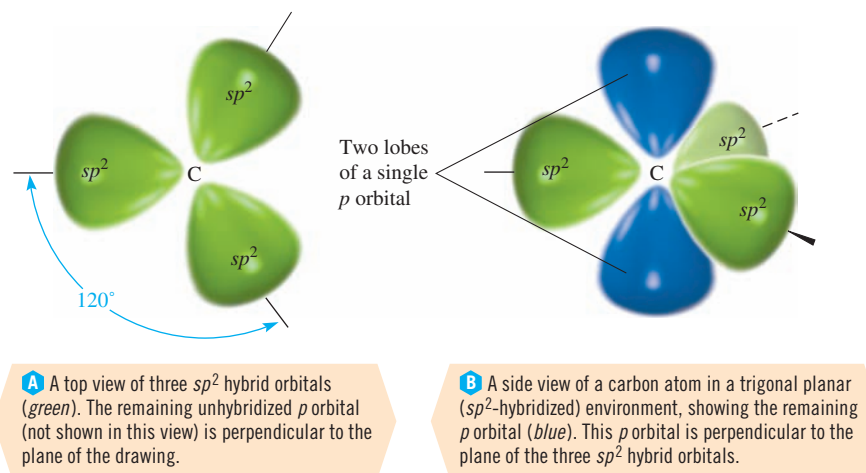


Figure 8-4 Orbitals on a sp^2 -hybridized carbon atom.

A pi bond can form *only* if there is *also* a sigma bond between the same two atoms. One sigma and one pi bond together make a double bond (Figure 8-5). The $1s$ orbitals (with one e^- each) of four hydrogen atoms overlap the remaining four sp^2 orbitals (with one e^- each) on the carbon atoms to form four C—H sigma bonds (Figure 8-6).

A double bond consists of one sigma bond and one pi bond.

As a consequence of the sp^2 hybridization of C atoms in carbon–carbon double bonds, each carbon atom is at the center of a trigonal plane. The p orbitals that overlap to form the π bond must be parallel to each other for effective overlap to occur. This adds the further restriction that these trigonal planes (sharing a common corner) must also be *coplanar*.

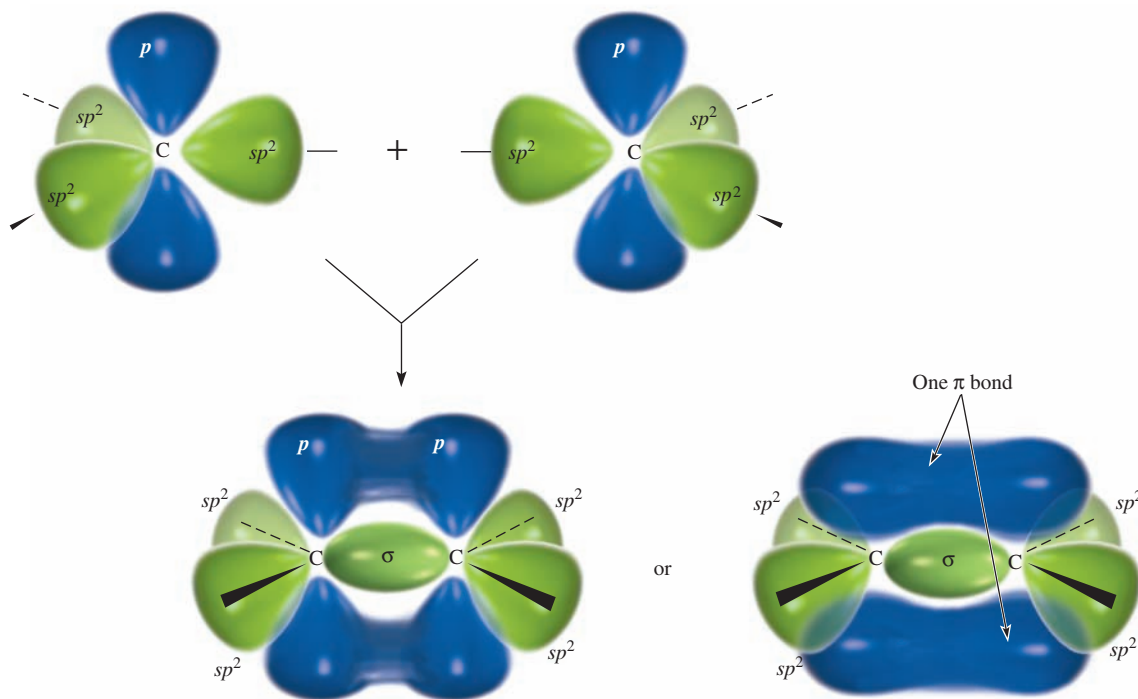


Figure 8-5 A schematic representation of the formation of a carbon–carbon double bond. Two sp^2 -hybridized carbon atoms form a sigma (σ) bond by overlap of two sp^2 orbitals (green) and a pi (π) bond by overlap of properly aligned p orbitals (blue). All orbitals are fatter than shown here.

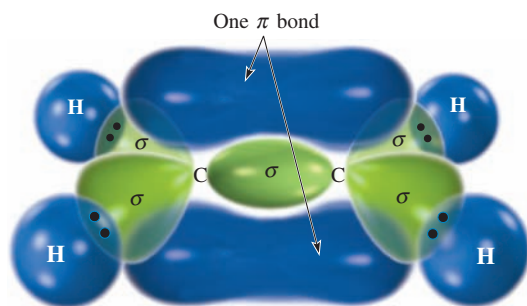
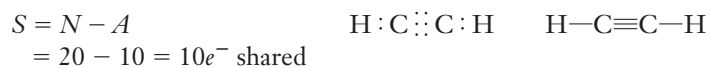


Figure 8-6 Four C—H σ bonds, one C—C σ bond (green), and one C—C π bond (blue) in the planar C_2H_4 molecule.

Thus, all four atoms attached to the doubly bonded C atoms lie in the same plane (see Figure 8-6). Many other important organic compounds contain carbon–carbon double bonds. Several are described in Chapter 23.

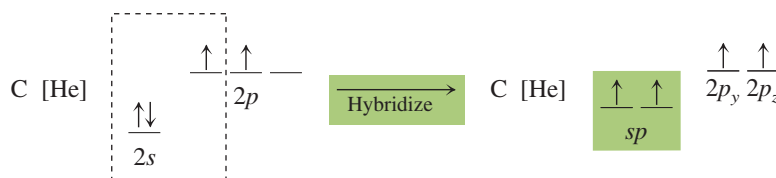
8-15 Compounds Containing Triple Bonds

One compound that contains a triple bond is ethyne (acetylene), C_2H_2 . Its Lewis formula is



The VSEPR theory predicts that the two electron groups around each carbon atom are 180° apart.

Each triple-bonded carbon atom has two electron groups, so valence bond theory postulates that each is sp hybridized (see Section 8-5). Let us designate the p_x orbitals as the ones involved in hybridization. Carbon has one electron in each sp hybrid orbital and one electron in each of the $2p_y$ and $2p_z$ orbitals (before bonding is considered) (Figure 8-7).



The two carbon atoms form one sigma bond by head-on overlap of the sp hybrid orbitals; each C atom also forms a sigma bond with one H atom. The sp hybrids on each atom are 180° apart. Thus, the entire molecule must be linear.



The unhybridized atomic $2p_y$ and $2p_z$ orbitals are perpendicular to each other and to the line through the centers of the two sp hybrid orbitals (Figure 8-8). The side-on overlap of the $2p_y$ orbitals on the two C atoms forms one pi bond; the side-on overlap of the $2p_z$ orbitals forms another pi bond.

A triple bond consists of one sigma bond and two pi bonds.



An important use of ethylene, C_2H_4 , is in the manufacture of polyethylene, a nonbreakable, nonreactive plastic.

► The three p orbitals in a set are indistinguishable. We can label the one involved in hybridization as " p_x " to help us visualize the orientations of the two unhybridized p orbitals on carbon.

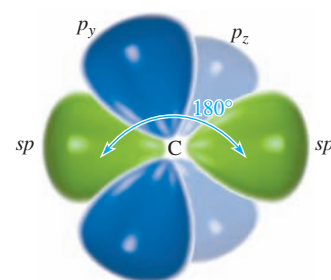


Figure 8-7 Diagram of the two linear hybridized sp orbitals (green) of an atom. These line in a straight line, and the two unhybridized p orbitals p_y and p_z (blue) line in the perpendicular plane and are perpendicular to each other.

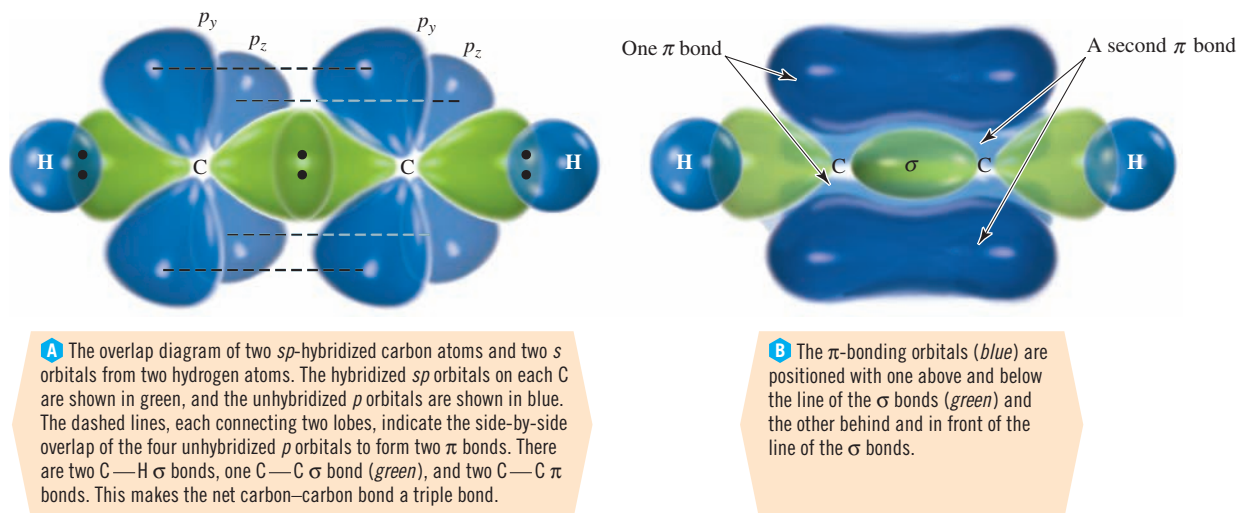


Figure 8-8 The acetylene molecule, C_2H_2 .

► In propyne, the C atom in the CH_3 group is sp^3 hybridized and at the center of a tetrahedral arrangement.

Some other molecules containing triply bonded atoms are nitrogen, $:N \equiv N:$; hydrogen cyanide, $H-C \equiv N$; and propyne, $CH_3-C \equiv C-H$. In each case, both atoms involved in the triple bonds are sp hybridized. In the triple bond, each atom participates in one sigma and two pi bonds. The C atom in carbon dioxide, $:\ddot{O} = C = \ddot{O}:$, must participate in two pi bonds (to two different O atoms) and also participates in two sigma bonds, so it is also sp hybridized, and the molecule is linear.

8-16 A Summary of Electronic and Molecular Geometries

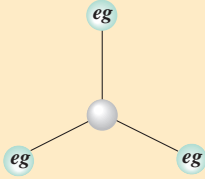
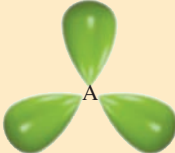
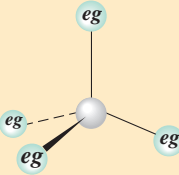
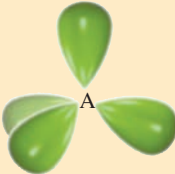
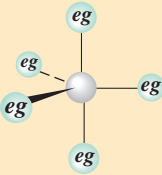
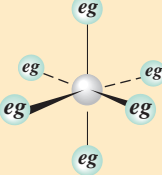
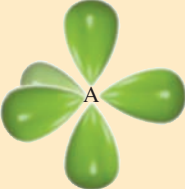
We have discussed several common types of polyatomic molecules and ions, and provided a reasonable explanation for the observed structures and polarities of these species. Table 8-4 provides a summation.

Our discussion of covalent bonding illustrates some important points:

1. Molecules and polyatomic ions have definite shapes.
2. The properties of molecules and polyatomic ions are determined to a great extent by their shapes. Incompletely filled electron shells and lone pairs of electrons on the central element are very important.
3. There are only *five* electronic geometries. All molecular geometries are simply special cases of these five basic geometries (Table 8-4).

Our ideas about chemical bonding have developed over many years. As experimental techniques for determining the *structures* of molecules have improved, our understanding of chemical bonding has also improved. Experimental observations on molecular geometry support our ideas about chemical bonding. The ultimate test for any theory is this: Can it correctly predict the results of experiments before they are performed? When the answer is yes, we have confidence in the theory. When the answer is no, the theory must be modified. Current theories of chemical bonding enable us to make predictions that are usually accurate.

Table 8-4 A Summary of Electronic and Molecular Geometries of Polyatomic Molecules and Ions

Electron Groups (eg) ^a	Electronic Geometry	Hybridization at Central Atom (Angles)	Hybridized Orbital Orientation	Examples	Molecular Geometry
2	 linear	sp (180°)		BeCl ₂ HgBr ₂ CdI ₂ CO ₂ ^b C ₂ H ₂ ^c	linear linear linear linear linear
3	 trigonal planar	sp^2 (120°)		BF ₃ BCl ₃ NO ₃ ^{-e} SO ₂ ^{d,e} NO ₂ ^{-d,e} C ₂ H ₄ ^f	trigonal planar trigonal planar trigonal planar angular (AB ₂ U) angular (AB ₂ U) planar (trig. planar at each C)
4	 tetrahedral	sp^3 (109.5°)		CH ₄ CCl ₄ NH ₄ ⁺ SO ₄ ²⁻ CHCl ₃ NH ₃ ^d SO ₃ ^{2-d} H ₃ O ⁺ ^d H ₂ O ^d	tetrahedral tetrahedral tetrahedral tetrahedral distorted tetrahedral pyramidal (AB ₃ U) pyramidal (AB ₃ U) pyramidal (AB ₃ U) angular (AB ₂ U ₂)
5	 trigonal bipyramidal	sp^3d (90°, 120°, 180°)		PF ₅ SbCl ₅ SF ₄ ^d ClF ₃ ^d XeF ₂ ^d I ₃ ^{-d}	trigonal bipyramidal trigonal bipyramidal seesaw (AB ₄ U) T-shaped (AB ₃ U ₂) linear (AB ₂ U ₃) linear (AB ₂ U ₃)
6	 octahedral	sp^3d^2 (90°, 180°)		SF ₆ SeF ₆ PF ₆ ^{-d} BrF ₅ ^d XeF ₄ ^d	octahedral octahedral octahedral square pyramidal (AB ₅ U) square planar (AB ₄ U ₂)

^aThe number of electron groups around the central atom. An electron group may be a single bond, a double bond, a triple bond, or a lone pair. These determine the electronic geometry, and thus the hybridization of the central atom.

^bContains two double bonds.

^cContains a triple bond.

^dCentral atom in molecule or ion has lone pair(s) of electrons.

^eBonding involves resonance.

^fContains one double bond.

KEY TERMS

Angular A term used to describe the molecular geometry of a molecule that has two atoms bonded to a central atom and one or more lone pairs on the central atom (AB_2U or AB_2U_2); also called *V-shaped* or *bent*.

Central atom An atom in a molecule or polyatomic ion that is bonded to more than one other atom.

Electron group A group of valence shell electrons that determines the electronic geometry on a central atom. Can be a single bond, double bond, triple bond, or lone pair.

Electronic geometry The geometric arrangement of the bonding and lone pair (unshared pair) electron groups around the central atom of a molecule or polyatomic ion. This arrangement minimizes the repulsions among the electron groups. Each electronic geometry implies a particular hybridization on the central atom.

Hybridization The mixing of a set of atomic orbitals on an atom to form a new set of hybrid orbitals with the same total electron capacity and with properties and energies intermediate between those of the original unhybridized orbitals.

Hybrid orbitals Orbitals formed on an atom by the process of hybridization.

Lewis formula A method of representing a molecule or formula unit by showing atoms and only outer-shell electrons; does not show shape.

Linear A term used to describe the electronic geometry around a central atom that has two electron groups. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to two atoms on opposite sides (180°) of the central atom (AB_2 or AB_2U_3).

Molecular geometry The arrangement of atoms (not electron groups) around a central atom of a molecule or polyatomic ion.

Octahedral A term used to describe the electronic geometry around a central atom that has six electron groups. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to six atoms at the corners of an octahedron (AB_6).

Octahedron (regular) A polyhedron with eight equal-sized, equilateral triangular faces and six apices (corners).

Overlap of orbitals The interaction of orbitals on different atoms in the same region of space.

Pi (π) bond A bond resulting from the side-on overlap of atomic orbitals, in which the regions of electron sharing are on opposite sides of and parallel to an imaginary line connecting the bonded atoms.

Seesaw A term used to describe the molecular geometry of a molecule or polyatomic ion that has four atoms bonded to a central atom and one lone pair on the central atom (AB_4U).

Sigma (σ) bond A bond resulting from the head-on overlap of atomic orbitals, in which the region of electron sharing is

along and (cylindrically) symmetrical to an imaginary line connecting the bonded atoms.

Square planar A term used to describe molecules and polyatomic ions that have one atom in the center and four atoms at the corners of a square.

Square pyramidal A term used to describe the molecular geometry of a molecule or polyatomic ion that has five atoms bonded to a central atom and one lone pair on the central atom (AB_5U).

Tetrahedral A term used to describe the electronic geometry around a central atom that has four electron groups. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to four atoms at the corners of a tetrahedron (AB_4).

Tetrahedron (regular) A polyhedron with four equal-sized, equilateral triangular faces and four apices (corners).

Trigonal bipyramid A six-sided polyhedron with five apices (corners), consisting of two pyramids sharing a common triangular base.

Trigonal bipyramidal A term used to describe the electronic geometry around a central atom that has five electron groups. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to five atoms at the corners of a trigonal bipyramid (AB_5).

Trigonal planar (also plane triangular) A term used to describe the electronic geometry around a central atom that has three electron groups. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to three atoms at the corners of an equilateral triangle (AB_3).

Trigonal pyramidal A term used to describe the molecular geometry of a molecule or polyatomic ion that has three atoms bonded to a central atom and one lone pair on the central atom (AB_3U).

T-shaped A term used to describe the molecular geometry of a molecule or polyatomic ion that has three atoms bonded to a central atom and two lone pairs on the central atom (AB_3U_2).

Valence bond (VB) theory Assumes that covalent bonds are formed when atomic orbitals on different atoms overlap and electrons are shared.

Valence shell The outermost occupied electron shell of an atom.

Valence shell electron pair repulsion (VSEPR) theory Assumes that valence electron pairs are arranged around the central element of a molecule or polyatomic ion so that there is maximum separation (and minimum repulsion) among electron groups.

EXERCISES

● Molecular Reasoning exercises

▲ More Challenging exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

VSEPR Theory: General Concepts

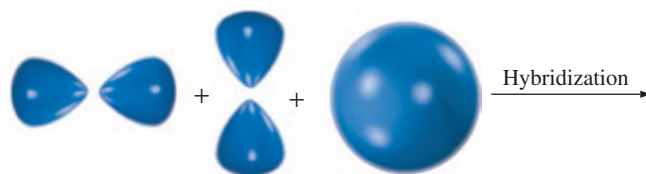
1. State in your own words the basic idea of the VSEPR theory.
2. (a) Distinguish between “lone pairs” and “bonding pairs” of electrons. (b) Which has the greater spatial requirement? How do we know this? (c) Indicate the order of increasing repulsions among lone pairs and bonding pairs of electrons.
3. ● What two shapes could a triatomic species have? How would the electronic geometries for the two shapes differ?
4. ▲ How are double and triple bonds treated when the VSEPR theory is used to predict molecular geometry? How is a single unshared electron treated?
5. ● Sketch the three different possible arrangements of the three B atoms around the central atom A for the molecule AB_3U_2 . Which of these structures correctly describes the molecular geometry? Why? What are the predicted ideal bond angles? How would observed bond angles deviate from these values?
6. ● Sketch the three different possible arrangements of the two B atoms around the central atom A for the molecule AB_2U_3 . Which of these arrangements predicts the most likely molecular geometry? Why?

Valence Bond Theory: General Concepts

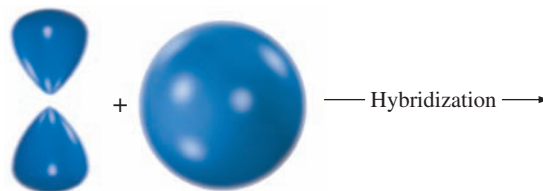
7. What are hybridized atomic orbitals? How is the theory of hybridized orbitals useful?
8. (a) What is the relationship between the electron groups on an atom and the number of its pure atomic orbitals that hybridize? (b) What is the relationship between the number of atomic orbitals that hybridize and the number of hybrid orbitals formed?
9. ● What hybridization is associated with these electronic geometries: trigonal planar, linear, tetrahedral, octahedral, trigonal bipyramidal?
10. Prepare sketches of the orbitals around atoms that are (a) sp , (b) sp^2 , (c) sp^3 , (d) sp^3d , and (e) sp^3d^2 hybridized. Show in the sketches any unhybridized p orbitals that might participate in multiple bonding.
11. ● What types of hybridization would you predict for molecules having the following general formulas? (a) AB_4 ; (b) AB_2U_3 ; (c) AB_3U ; (d) ABU_4 ; (e) ABU_3 .
12. ● Repeat Exercise 11 for (a) ABU_5 ; (b) AB_2U_4 ; (c) AB_3 ; (d) AB_3U_2 ; (e) AB_5 .
13. ● (a) What is the maximum number of bonds that an atom can form without expanding its valence shell? (b) What must be true of the electron configuration

of an element for it to be able to expand its valence shell? (c) Which of the following elements can expand its valence shell? N, O, F, P, S, Cl, Xe.

14. The formation of what set of hybrid orbitals is being shown in the following incomplete sketch? Complete the sketch by drawing the hybrid orbitals formed.



15. The formation of what set of hybrid orbitals is being shown in the following incomplete sketches? Complete the sketch by drawing the hybrid orbitals formed.



16. What angles are associated with orbitals in the following sets of hybrid orbitals? (a) sp ; (b) sp^2 ; (c) sp^3 ; (d) sp^3d ; (e) sp^3d^2 . Sketch each set.
17. ● What are the primary factors on which we base a decision on whether the bonding in a molecule is better described in terms of overlap of pure atomic orbitals or overlap involving hybridized atomic orbitals?
18. ● The elements in Group 2A form compounds, such as $Cl-Be-Cl$, that are linear and, therefore, nonpolar. What is the hybridization at the central atoms?
19. ● The elements in Group 3A form compounds, such as $AlCl_3$, that are planar and, therefore, nonpolar. What is the hybridization at the central atoms?

Electronic and Molecular Geometry

20. Under what conditions is molecular (or ionic) geometry identical to electronic geometry about a central atom?
21. Distinguish between electronic geometry and molecular geometry.
22. ● Identify the central atom (or atoms) in each of the following compounds or ions: (a) HCO_3^- ; (b) SiO_2 ; (c) SO_3 ; (d) $Al(OH)_4^-$; (e) $BeBr_2$; (f) $(CH_3)_4Pb$.

● Molecular Reasoning exercises

▲ More Challenging exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

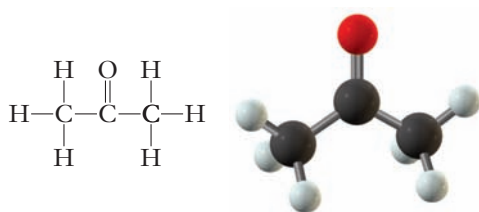
23. Identify the central atom in each of the following compounds or ions: (a) SO_4^{2-} ; (b) NH_3 ; (c) NH_4^+ ; (d) AlCl_3 ; (e) CH_3NH_2 ; (f) CdCl_2 .
24. Write a Lewis formula for each of the following species. Indicate the number of electron groups and the electronic and molecular or ionic geometries. (a) CdCl_2 ; (b) SnCl_4 ; (c) BrF_3 ; (d) SbF_6^- .
25. Write a Lewis formula for each of the following species. Indicate the number of electron groups and the electronic and molecular or ionic geometries. (a) BF_3 ; (b) SO_2 ; (c) IO_3^- ; (d) SiCl_4 ; (e) SeF_6 .
26. (a) What would be the ideal bond angles in each molecule or ion in Exercise 24? (b) How do these differ, if at all, from the actual values? Why?
27. (a) What would be the ideal bond angles in each molecule or ion in Exercise 25? (b) Are these values greater than, less than, or equal to the actual values? Why?
28. Write the Lewis formula and identify the electronic geometry and molecular geometry for each polyatomic species in the following equations:
- (a) $\text{H}^+ + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+$
 (b) $\text{NH}_3 + \text{H}^+ \longrightarrow \text{NH}_4^+$
29. Pick the member of each pair that you would expect to have the smaller bond angles, if different, and explain why. (a) SF_2 and SO_2 ; (b) BF_3 and BCl_3 ; (c) SiF_4 and SF_4 ; (d) NF_3 and OF_2 .
30. Draw a Lewis formula, sketch the three-dimensional shape, and name the electronic and ionic geometries for the following polyatomic ions. (a) H_3O^+ ; (b) PCl_6^- ; (c) PCl_4^- ; (d) SbCl_4^+ .
31. As the name implies, the interhalogens are compounds that contain two halogens. Write Lewis formulas and three-dimensional structures for the following. Name the electronic and molecular geometries of each. (a) BrF_3 ; (b) BrF ; (c) BrF_5 .
32. (a) Write a Lewis formula for each of the following molecules: SiF_4 , SF_4 , XeF_4 . (b) Contrast the molecular geometries of these three molecules. Account for differences in terms of the VSEPR theory.
33. Draw a Lewis structure for each of the following molecules or ions: (a) BrF_5 ; (b) IF_3 ; (c) IBr_2^- ; (d) BrF_2^+ .
34. Write the Lewis formulas and predict the shapes of (a) I_3^- ; (b) TeCl_4 ; (c) XeO_3 ; (d) NOBr (N is the central atom); (e) NO_2Cl (N is the central atom); (f) SOCl_2 (S is the central atom).
35. Describe the shapes of these polyatomic ions: (a) BO_3^{3-} ; (b) AsO_4^{3-} ; (c) SO_3^{2-} ; (d) NO_3^- .
36. Would you predict a nitrogen–oxygen bond to have the same magnitude of bond polarity as a hydrogen–oxygen bond? Explain your answer.
37. Which of the following molecules are polar? Why? (a) CH_4 ; (b) CH_3Br ; (c) CH_2Br_2 ; (d) CHBr_3 ; (e) CBr_4 .
38. Which of the following molecules are polar? Why? (a) CdI_2 ; (b) BCl_3 ; (c) AsCl_3 ; (d) H_2O ; (e) SF_6 .
39. Which of the following molecules are nonpolar? Justify your answer. (a) SO_3 ; (b) IF ; (c) Cl_2O ; (d) NF_3 ; (e) CHCl_3 .
40. Each of these molecules has fluorine atoms attached to an atom from Group 1A or 3A to 6A. Draw the Lewis structure for each one and then describe the electron-pair geometry and the molecular geometry. Comment on similarities and differences in the series. (a) BF_3 ; (b) CF_4 ; (c) NF_3 ; (d) OF_2 ; (e) HF .
41. In what two major ways does the presence of lone pairs of valence electrons affect the polarity of a molecule? Describe two molecules for which the presence of lone pairs on the central atom helps to make the molecules polar. Can you think of a bonding arrangement that has lone pairs of valence electrons on the central atom but that is nonpolar? Describe a molecule with this arrangement.
42. Is the phosphorus–chlorine bond in phosphorus trichloride a polar bond? Is phosphorus trichloride a polar molecule? Explain.
43. Is the phosphorus–chlorine bond in phosphorus pentachloride a polar bond? Is phosphorus pentachloride a polar molecule? Explain.
44. Write the Lewis formula for each of the following. Indicate which bonds are polar. (See Table 5-3.) Indicate which molecules are polar. (a) CS_2 ; (b) AlF_3 ; (c) H_2S ; (d) SnF_2 .
45. Write the Lewis formula for each of the following. Indicate which bonds are polar. (See Table 5-3.) Indicate which molecules are polar. (a) OF_2 ; (b) CH_4 ; (c) H_2SO_4 ; (d) SnF_4 .

Valence Bond Theory

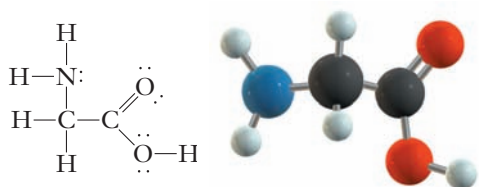
46. Describe the orbital overlap model of covalent bonding.
47. Briefly summarize the reasoning by which we might have predicted that the formula of the simplest stable hydrocarbon would be CH_2 , if we did not consider hybridization. Would this species satisfy the octet rule?
48. What is the hybridization of the central atom in each of the following? (a) NCl_3 ; (b) molecular AlCl_3 ; (c) CF_4 ; (d) SF_6 ; (e) IO_4^- .
49. What is the hybridization of the central atom in each of the following? (a) IF_4^- ; (b) SiO_4^{4-} ; (c) AlH_4^- ; (d) NH_4^+ ; (e) PCl_3 ; (f) ClO_3^- .
50. (a) Describe the hybridization of the central atom in each of these covalent species. (i) CHCl_3 ; (ii) CH_2Cl_2 ; (iii) NF_3 ; (iv) PO_4^{3-} ; (v) IF_6^+ ; (vi) SiF_6^{2-} . (b) Give the shape of each species.
51. Describe the hybridization of the underlined atoms in C_2F_6 , C_2F_4 , and $(\text{H}_2\text{N})_2\text{CO}$.
52. Prepare a sketch of the molecule $\text{CH}_3\text{CCl}=\text{CH}_2$ showing orbital overlaps. Identify the type of hybridization of atomic orbitals on each carbon atom.
53. What is the maximum number of hybrid orbitals that a carbon atom may form? What is the minimum number? Explain briefly.

54. Predict the hybridization at each carbon atom in each of the following molecules.

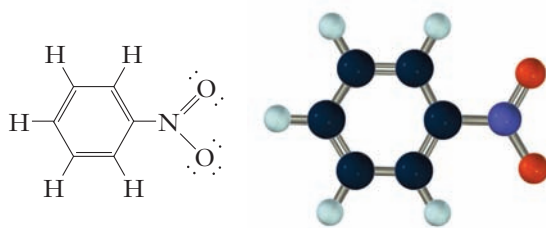
(a) acetone (a common solvent)



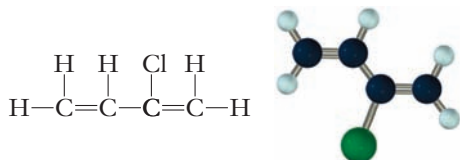
(b) glycine (an amino acid)



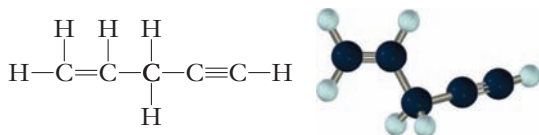
(c) nitrobenzene¹



(d) chloroprene (used to make neoprene, a synthetic rubber)

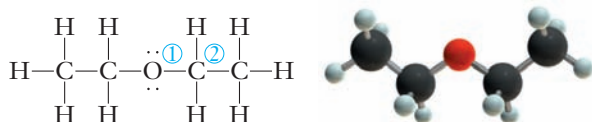


(e) 4-penten-1-yne

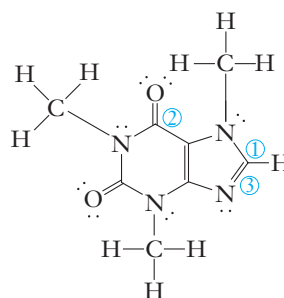


55. Predict the hybridization at the numbered atoms (①, ② and so on) in the following molecules and predict the approximate bond angles at those atoms.

(a) diethyl ether, an anesthetic



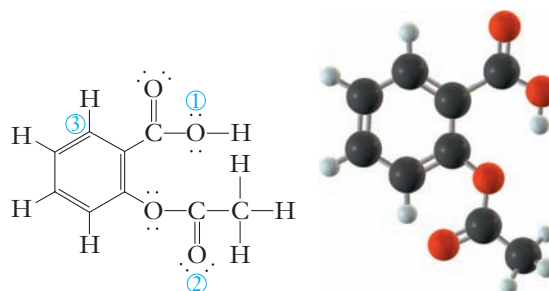
(b) caffeine, a stimulant in coffee and in many over-the-counter medicinals¹



Charles D. Winters

Coffee

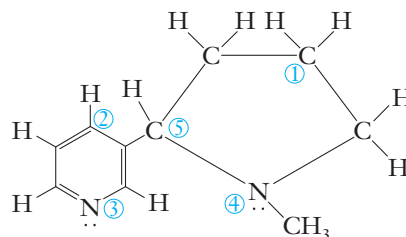
(c) acetylsalicylic acid (aspirin)¹



Charles D. Winters

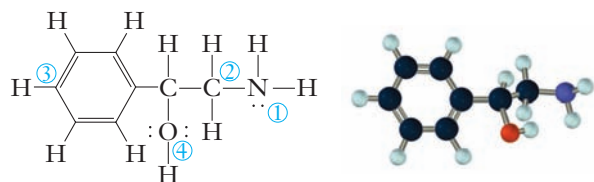
Aspirin

(d) nicotine¹

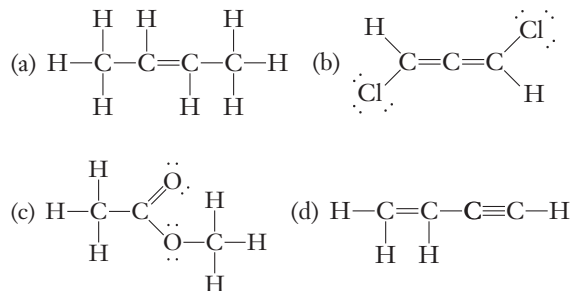


¹In these kinds of structural drawings, each intersection of lines represents a C atom.

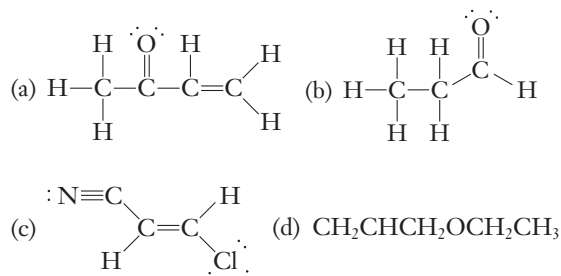
(e) ephedrine, a nasal decongestant¹



56. Prepare sketches of the overlaps of the following atomic orbitals: (a) s with s ; (b) s with p along the bond axis; (c) p with p along the bond axis (head-on overlap); (d) p with p perpendicular to the bond axis (side-on overlap).
57. Prepare a sketch of the cross section (through the atomic centers) taken between two atoms that have formed (a) a single σ bond; (b) a double bond consisting of a σ bond and a π bond; and (c) a triple bond consisting of a σ bond and two π bonds.
58. How many sigma and how many pi bonds are there in each of the following molecules?



59. How many sigma bonds and how many pi bonds are there in each of the following molecules?

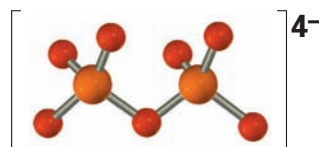


60. In each of these ions, three oxygen atoms are attached to a central atom. Draw the Lewis structure for each one, and then describe the electron-pair geometry and the ionic geometry. Comment on similarities and differences in the series. (a) BO_3^{3-} ; (b) CO_3^{2-} ; (c) SO_3^{2-} ; (d) ClO_3^- .
61. Write Lewis formulas for molecular oxygen and ozone. Assuming that all of the valence electrons in the oxygen atoms are in hybrid orbitals, what would be the hybridization of the oxygen atoms in each substance? Prepare sketches of the molecules.

62. Draw a Lewis formula and a three-dimensional structure for each of the following polycentered molecules. Indicate hybridizations and bond angles at each carbon atom. (a) butane, C_4H_{10} ; (b) propene, $\text{H}_2\text{C}=\text{CHCH}_3$; (c) 1-butyne, $\text{HC}\equiv\text{CCH}_2\text{CH}_3$; (d) acetaldehyde, CH_3CHO .
63. How many σ bonds and how many π bonds are there in each of the molecules of Exercise 62?
64. (a) Describe the hybridization of N in each of these species. (i) NH_3 ; (ii) NH_4^+ ; (iii) $\text{HN}=\text{NH}$; (iv) $\text{:N}\equiv\text{HC}$; (v) $\text{H}_2\text{N}-\text{NH}_2$. (b) Give an orbital description for each species, specifying the location of any lone pairs and the orbitals used for the multiple bonds.
65. Write the Lewis formulas and predict the hybrid orbitals and the shapes of these polyatomic ions and covalent molecules: (a) HgCl_2 ; (b) BF_3 ; (c) BF_4^- ; (d) SbCl_5 ; (e) SbF_6^- .
66. (a) What is the hybridization of each C in these molecules? (i) $\text{H}_2\text{C}=\text{O}$; (ii) $\text{HC}\equiv\text{N}$; (iii) $\text{CH}_3\text{CH}_2\text{CH}_3$; (iv) ketene, $\text{H}_2\text{C}=\text{C}=\text{O}$. (b) Describe the shape of each molecule.
67. The following fluorides of xenon have been well characterized: XeF_2 , XeF_4 , and XeF_6 . (a) Write Lewis formulas for these substances, and decide what type of hybridization of the Xe atomic orbitals has taken place. (b) Draw all of the possible atomic arrangements of XeF_2 , and discuss your choice of molecular geometry. (c) What shape do you predict for XeF_4 ?
68. Iodine and fluorine form a series of interhalogen molecules and ions. Among these are IF (minute quantities observed spectroscopically), IF_3 , IF_4^- , IF_5 , IF_6^- , and IF_7 . (a) Write Lewis formulas for each of these species. (b) Identify the type of hybridization that the orbitals of the iodine atom have undergone in the first four substances. (c) Identify the shape of the molecule or ion represented by the first four formulas.

Mixed Exercises

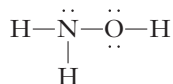
69. In the pyrophosphate ion, $\text{P}_2\text{O}_7^{4-}$, one oxygen atom is bonded to both phosphorus atoms.



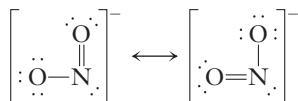
Write a Lewis formula, and sketch the three-dimensional shape of the ion. Describe the electronic and molecular geometries with respect to the central O atom and with respect to each P atom.

¹In these kinds of structural drawings, each intersection of lines represents a C atom.

70. Briefly discuss the bond angles in the hydroxylamine molecule in terms of the ideal geometry and the small changes caused by electron-pair repulsions.

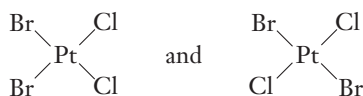


71. Repeat Exercise 70 for the nitrite ion.



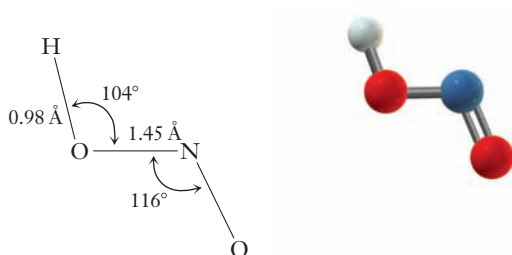
72. The methyl free radical $\cdot\text{CH}_3$ has bond angles of about 120° , whereas the methyl carbanion $:\text{CH}_3^-$ has bond angles of about 109° . What can you infer from these facts about the repulsive force exerted by an unpaired, unshared electron as compared with that exerted by an unshared pair of electrons?

73. Two Lewis structures can be written for the square planar molecule PtCl_2Br_2 .



Show how a difference in dipole moments can distinguish between these two possible structures.

74. (a) Describe the hybridization of N in NO_2^+ and NO_2^- .
(b) Predict the bond angle in each case.
75. The skeleton and a ball-and-stick model for the nitrous acid molecule, HNO_2 , are shown here. Draw the Lewis formula. What are the hybridizations at the middle O and N atoms?



76. Describe the change in hybridization that occurs at the central atom of the reactant at the left in each of the following reactions.
- $\text{PF}_5 + \text{F}^- \longrightarrow \text{PF}_6^-$
 - $2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2$
 - $\text{AlI}_3 + \text{I}^- \longrightarrow \text{AlI}_4^-$
 - What change in hybridization occurs in the following reaction? $:\text{NH}_3 + \text{BF}_3 \longrightarrow \text{H}_3\text{N}:\text{BF}_3$

77. Predict the geometry of the following species: (a) NNO ; (b) ONCl ; (c) NH_4^+ ; (d) O_3 .

78. What hybridizations are predicted for the central atoms in molecules having the formulas AB_2U_2 and AB_3U ? What are the predicted bond angles for these molecules? The observed bond angles for representative substances are:

H_2O	104.5°	NH_3	106.7°
H_2S	92.2°	PH_3	93.7°
H_2Se	91.0°	AsH_3	91.8°
H_2Te	89.5°	SbH_3	91.3°

What would be the predicted bond angle if no hybridization occurred? What conclusion can you draw concerning the importance of hybridization for molecules of compounds involving elements with higher atomic numbers?

Conceptual Exercises

79. Draw and explain the difference in the three-dimensional shapes of $\text{CH}_3\text{CH}_2\text{CH}_3$ and CH_3COCH_3 .
80. Complete the following table.

Molecule or Ion	Electronic Geometry	Molecular Geometry	Hybridization of the Sulfur Atom
SO_2			
SCl_2			
SO_3			
SO_3^{2-}			
SF_4			
SO_4^{2-}			
SF_5^+			
SF_6			

81. Compare the shapes of the following pairs of molecules: (a) H_2CO and CH_4 ; (b) PbCl_4 and PbO_2 ; (c) CH_4 and PbCl_4 .
82. (a) Why is trifluoromethane (HCF_3) polar and tetrafluoromethane (CF_4) nonpolar? (b) Give an example of a linear triatomic molecule that is polar. (c) What can be said about the distribution of valence electrons in a polar molecule?

83. Complete the following table regarding hybridized orbitals:

Hybridized Atomic Orbitals	<i>p</i> Orbitals Not Hybridized	Hybridization	Electronic Geometry
one <i>s</i> , three <i>p</i> 's	–	sp^3	tetrahedral
one <i>s</i> , two <i>p</i> 's		sp^2	
	2 <i>p</i>		linear
one <i>s</i> , three <i>p</i> 's, one <i>d</i>	–		
		sp^3d^2	octahedral

84. (a) What are the five different electronic geometries? (b) How many molecular geometries are described in this chapter? (c) An ion or molecule having the following would lead one to predict what molecular geometry of each combination?

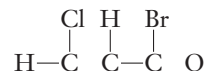
- 2 bonded atoms, 1 lone pair
- 3 bonded atoms, 1 lone pair
- 2 bonded atoms, 2 lone pairs
- 4 bonded atoms, 1 lone pair
- 3 bonded atoms, 2 lone pairs
- 2 bonded atoms, 3 lone pairs
- 5 bonded atoms, 1 lone pair
- 4 bonded atoms, 2 lone pairs

85. What advantages does the VSEPR model of chemical bonding have compared with Lewis formulas?
86. What evidence could you present to show that two carbon atoms joined by a single sigma bond are able to rotate about an axis that coincides with the bond, but two carbon atoms bonded by a double bond cannot rotate about an axis along the double bond?

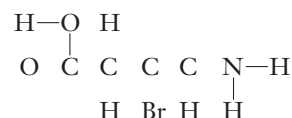
Building Your Knowledge

87. Sketch three-dimensional representations of the following molecules and indicate the direction of any net dipole for each molecule: (a) CH_4 ; (b) CH_3Cl ; (c) CH_2Cl_2 ; (d) CHCl_3 ; (e) CCl_4 .
88. Carbon forms two common oxides, CO and CO_2 . It also forms a third (very uncommon) oxide, carbon suboxide, C_3O_2 , which is linear. The structure has terminal oxygen atoms on both ends. Write the Lewis formula for C_3O_2 . How many electron groups are there about each of the three carbon atoms?

89. Draw the Lewis formula of an ammonium ion. Describe the formation of the ammonium ion from ammonia plus H^+ . Does the hybridization of orbitals on nitrogen change during the formation of the ammonium ion? Do the bond angles change?
90. The following is an incomplete Lewis formula for a molecule. This formula has all the atoms at the correct places, but it is missing several valence electrons. Complete this Lewis formula, including lone pairs.



91. The following is an incomplete Lewis formula for a molecule. This formula has all the atoms at the correct places, but it is missing several valence electrons. Complete this Lewis formula, including lone pairs.



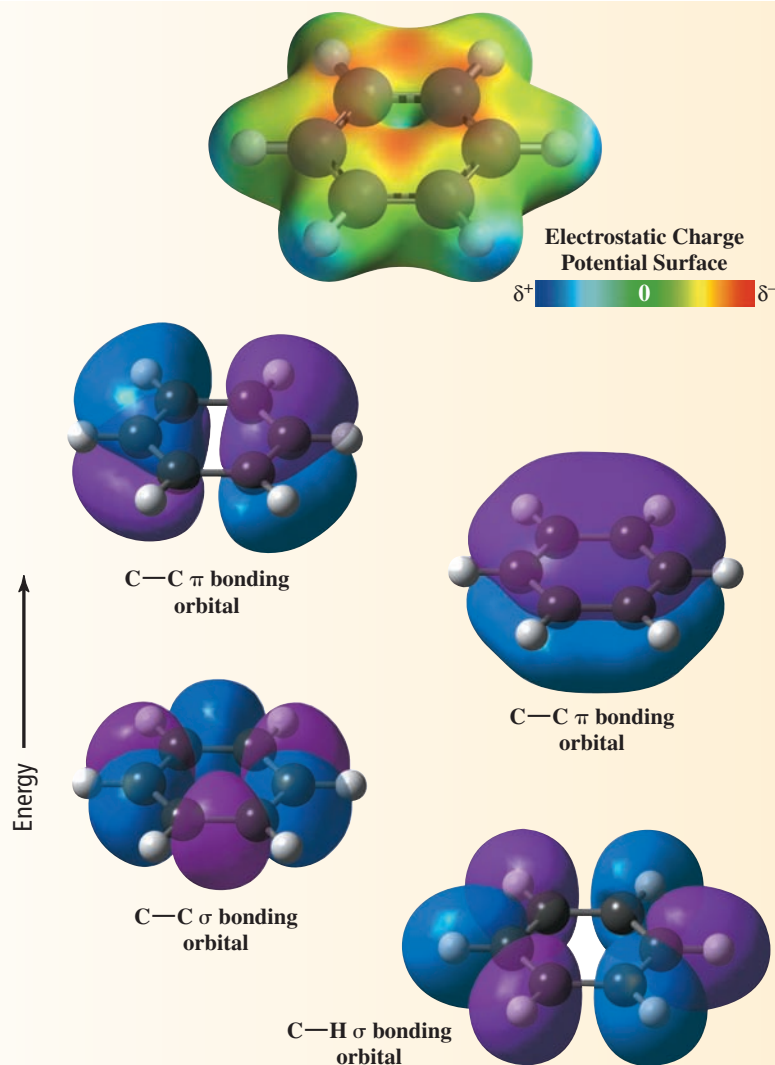
Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

92. Open www.winter.group.shef.ac.uk/orbitron or a site that describes atomic orbitals. (a) Click on $2p$. What is said to be wrong with the “figure-of-eight” style of drawing of *p* orbitals that is found in most textbooks? (b) What is the difference between $2p$ and $3p$ orbitals? (c) Click on $4f$. Draw one of the $4f$ orbitals that contains eight easily distinguished lobes. (d) Click on $5g$. How many lobes does the $5g_{xy^3}$ orbital contain?
93. Use the *Handbook of Chemistry and Physics* or a suitable web page to find dipole moments. What do the dipole moments for SnI_4 and TiCl_4 tell us about the shapes of these compounds?
94. Predict whether the dipole moment of each of the following molecules should be zero, nearly zero, or significantly larger than zero. Then use the *Handbook of Chemistry and Physics* to find their correct dipole moment values. Compare your predictions with the values found in the Handbook or at a suitable website. (a) acetylene; (b) trichloromethane (chloroform); (c) dibromomethane; (d) methanol (CH_3OH); (e) ethanol ($\text{CH}_3\text{CH}_2\text{OH}$).

Molecular Orbitals in Chemical Bonding

9



The lower part of the figure shows some of the molecular orbitals for benzene (C_6H_6) that contribute to the various C—H and C—C σ - and π -bonding interactions. The purple and blue colors represent the different phases (+ or -) for the wave functions that define the orbitals. The top image is a ball-and-stick model of benzene superimposed on an electrostatic charge potential surface showing relative charges. These images were all generated from a computer program (Gaussian 09) that calculates the electronic structure of molecules and plots the molecular orbitals.

© Cengage Learning/George Stanley

OUTLINE

- 9-1 Molecular Orbitals
- 9-2 Molecular Orbital Energy Level Diagrams
- 9-3 Bond Order and Bond Stability
- 9-4 Homonuclear Diatomic Molecules
- 9-5 Heteronuclear Diatomic Molecules
- 9-6 Delocalization and the Shapes of Molecular Orbitals

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Describe the basic concepts of molecular orbital theory
- ▶ Relate the shapes and overlap of atomic orbitals to the shapes and energies of the resulting molecular orbitals
- ▶ Distinguish among bonding, antibonding, and nonbonding orbitals
- ▶ Apply the Aufbau Principle to find molecular orbital descriptions for homonuclear diatomic molecules and ions
- ▶ Apply the Aufbau Principle to find molecular orbital descriptions for heteronuclear diatomic molecules and ions with small $\Delta(\text{EN})$ values
- ▶ Find the bond order in diatomic molecules and ions
- ▶ Relate bond order to bond stability
- ▶ Use the MO concept of delocalization for molecules for which valence bond theory would postulate resonance

We have described bonding and molecular geometry in terms of valence bond (VB) theory. In valence bond theory, we postulate that bonds result from the sharing of electrons in overlapping orbitals of different atoms. We describe electrons in overlapping orbitals of different atoms as being localized in the bonds between the two atoms involved. We use hybridization to help account for the geometry of a molecule. In valence bond theory, however, we view each orbital as belonging to an individual atom.

In **molecular orbital (MO) theory**, we postulate that

the combination of atomic orbitals on different atoms forms **molecular orbitals (MOs)** so that electrons in them belong to the molecule as a whole.

Valence bond and molecular orbital theories are alternative descriptions of chemical bonding. They have strengths and weaknesses, so they are complementary. Valence bond theory is descriptively attractive, and it lends itself well to visualization. Molecular orbital theory gives better descriptions of electron cloud distributions, bond energies, and magnetic properties, but its results are not as easy to visualize.

The valence bond description of bonding in the O_2 molecule involves a double bond.



This shows no unpaired electrons, so it predicts that O_2 is diamagnetic. Experiments show, however, that O_2 is paramagnetic; therefore, it must have unpaired electrons. Thus, the valence bond description is not consistent with experimental fact, so it cannot be accepted as a description of the bonding in O_2 . Molecular orbital theory accounts for the fact that O_2 has two unpaired electrons. This ability of MO theory to explain the paramagnetism of O_2 helped to establish it as a major theory of bonding. We will develop some of the ideas of MO theory and apply them to some molecules and polyatomic ions.

9-1 Molecular Orbitals

We learned in Chapter 4 that each solution to the Schrödinger equation, called a wave function, represents an atomic orbital. In valence bond theory (see Chapter 5), the mathematical picture of a hybrid orbital can be generated by combining the wave functions that describe two or more atomic orbitals (AOs) on a *single* atom. Similarly, combining wave functions that describe atomic orbitals on *separate* atoms generates mathematical descriptions of molecular orbitals.

An orbital has physical meaning only when we square its wave function to describe the electron density. Thus, the overall sign on the wave function that describes a *single* atomic orbital is not important, but when we *combine* two orbitals, the signs of the wave functions become very significant. When waves are combined, they may interact either constructively or destructively (Figure 9-1). Likewise, when two atomic orbitals overlap, they can

- ▶ In some polyatomic molecules, a molecular orbital may extend over only a fraction of the molecule.
- ▶ Polyatomic ions such as CO_3^{2-} , SO_4^{2-} , and NH_4^+ can be described by the molecular orbital approach.
- ▶ Species with all electrons paired are diamagnetic; species that contain any unpaired electrons are paramagnetic (see Section 4-20).

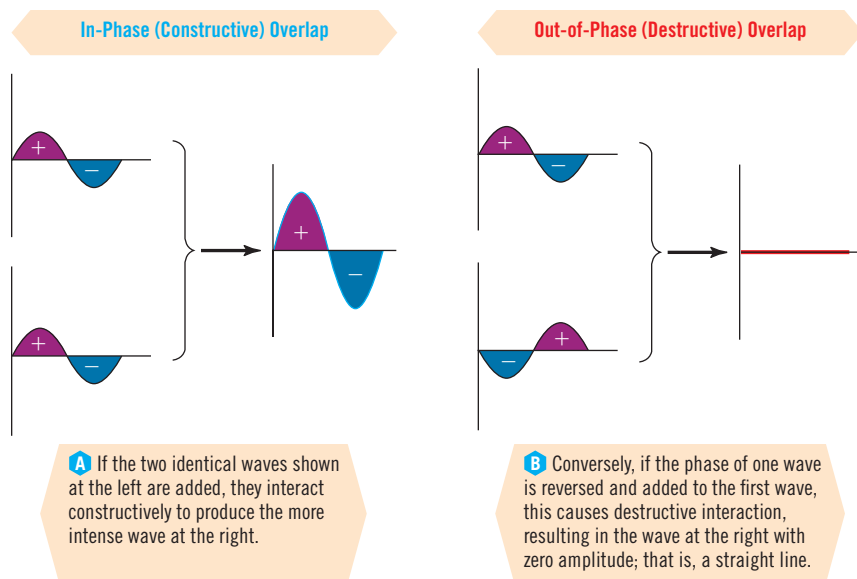


Figure 9-1 An illustration of constructive and destructive interference of waves.

be in phase or out of phase. When they overlap in phase, constructive interaction occurs in the region between the nuclei, and a **bonding molecular orbital** is produced. The energy of the bonding orbital is always lower (more stable) than the energies of the combining orbitals. When the orbitals overlap out of phase, destructive interaction reduces the probability of finding electrons in the region between the nuclei, and an **antibonding molecular orbital** is produced. This is higher in energy (less stable) than the original atomic orbitals, leading to a repulsion between the two atoms. The overlap of two atomic orbitals always produces two MOs: one bonding and one antibonding.

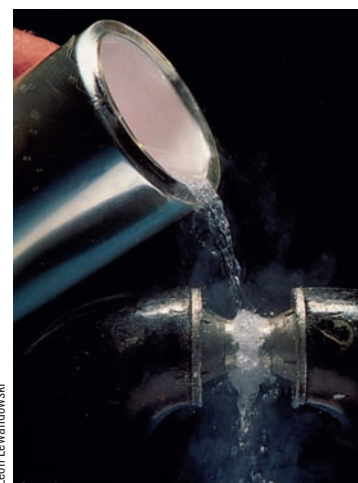
In a bonding molecular orbital, the electron density is high *between* the two atoms, where it stabilizes the arrangement by attracting both nuclei. Electrons are *more* stable (have lower energy) in bonding molecular orbitals than in the individual atoms. By contrast, an antibonding orbital has a node (a region of zero electron density) between the nuclei; this causes the nuclei to repel one another more strongly, which makes the arrangement less stable. Placing electrons in antibonding orbitals requires an increase in their energy, which makes them *less* stable than in the individual atoms.

To summarize, electrons in *bonding* orbitals tend to *stabilize* a molecule or ion; electrons in *antibonding* orbitals tend to *destabilize* a molecule or ion. The relative number of electrons in bonding versus antibonding orbitals determines the *overall stability* of the molecule or ion.

We can illustrate this basic principle by considering the combination of the $1s$ atomic orbitals *on two different atoms* (Figure 9-2). When these orbitals are occupied by electrons, the shapes of the orbitals are plots of electron density. These plots show the regions in molecules where the probabilities of finding electrons are the greatest.

In the bonding orbital, the two $1s$ orbitals have reinforced each other in the region between the two nuclei by in-phase (constructive) overlap of their electron waves. In the antibonding orbital, they have canceled each other in this region by out-of-phase (destructive) overlap of their electron waves. We designate both molecular orbitals as **sigma (σ) molecular orbitals** (which indicates that they are cylindrically symmetrical about the internuclear axis). We use subscripts to indicate the atomic orbitals that have been combined. The asterisk (*) denotes an antibonding orbital. Thus, two $1s$ orbitals produce a σ_{1s} (read “sigma- $1s$ ”) bonding orbital and a σ_{1s}^* (read “sigma- $1s$ -star”) antibonding orbital. The right-hand side of Figure 9-2 shows the relative energy levels of these orbitals. All sigma antibonding orbitals have nodal planes bisecting the internuclear axis. A **node**, or **nodal plane**, is a region in which the probability of finding electrons is zero.

For any two sets of p orbitals on two different atoms, corresponding orbitals such as p_x orbitals can overlap *head-on*. This gives σ_p and σ_p^* orbitals, as shown in Figure 9-3 for the



Liquid oxygen is attracted to the poles of a powerful magnet, indicating that it is paramagnetic. An early triumph of molecular orbital theory was its ability to account for the observed paramagnetism of oxygen, O_2 . According to earlier theories, O_2 was expected to be diamagnetic, that is, to have only paired electrons.

► How we name the axes is arbitrary. Here we designate the internuclear axis as the x direction.

Unless otherwise noted, all content on this page is © Cengage Learning.

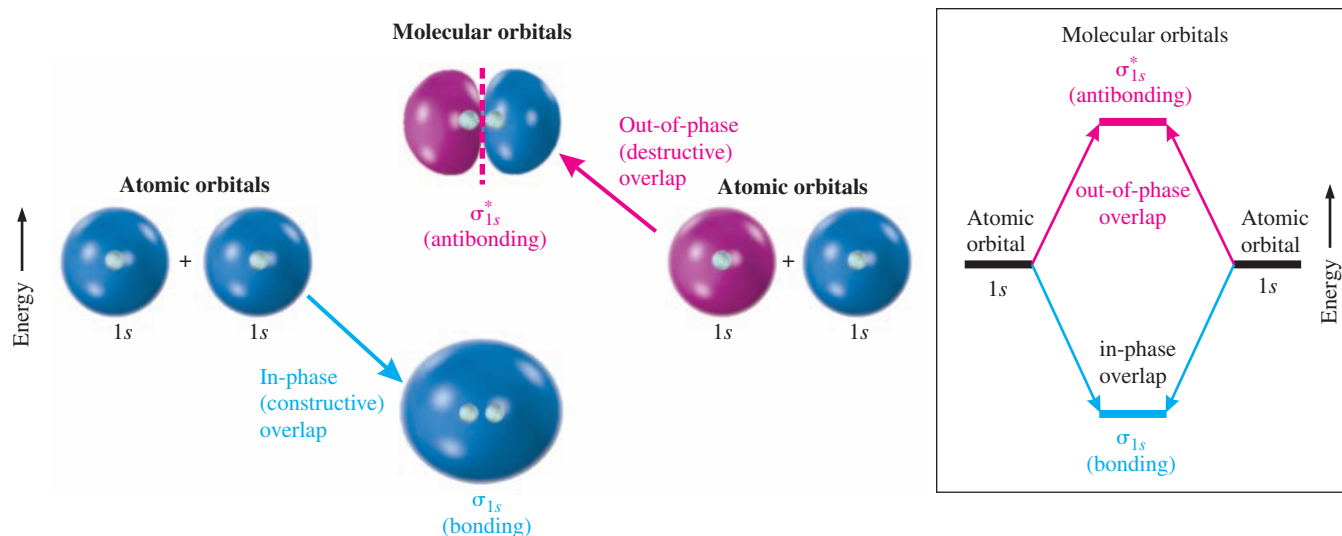


Figure 9-2 Molecular orbital diagram for the combination of the 1s atomic orbitals (AOs) on two identical atoms to form two new molecular orbitals (MOs). One is a *bonding* orbital, σ_{1s} , resulting from the constructive (in-phase) overlap of 1s wave functions that have the same mathematical sign (both + or both -, represented here by the same color). The other is an *antibonding* orbital, σ_{1s}^* , at higher energy resulting from the destructive (out-of-phase) overlap of 1s wave functions with opposite signs (represented here by different orbital colors), resulting in a repulsive force between the atoms. In all σ -type MOs, the electron density is symmetrical about an imaginary line connecting the two nuclei. The nodal plane between the atoms in the σ_{1s}^* is indicated by a dashed red line.

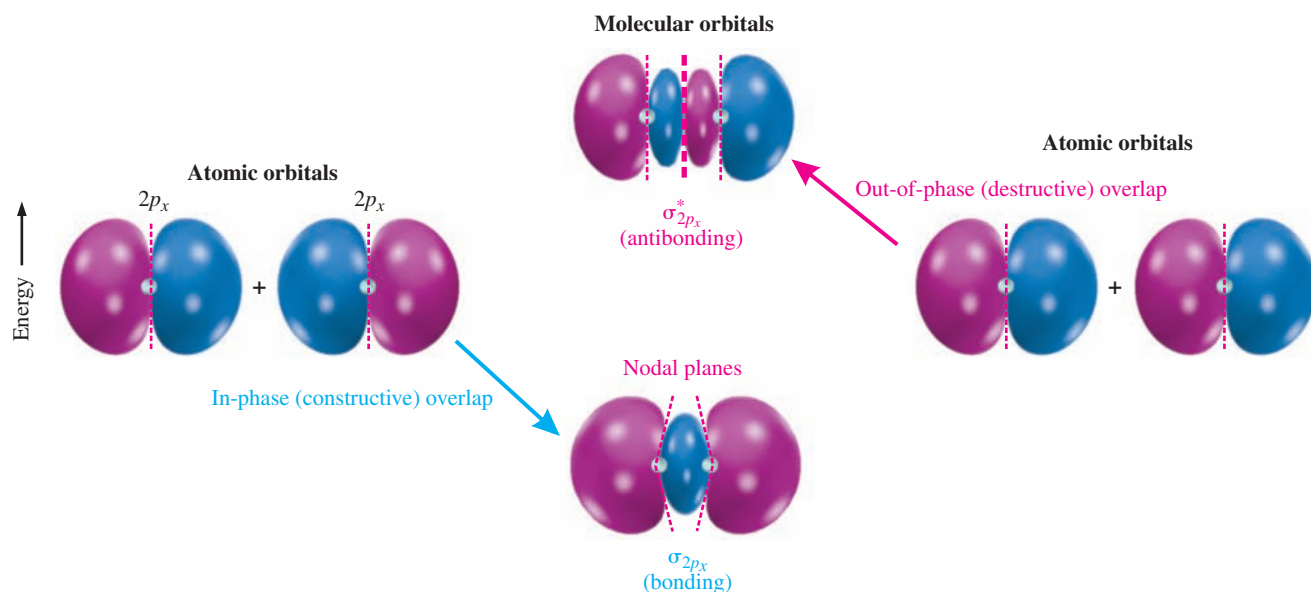


Figure 9-3 Production of σ_{2p_x} and $\sigma_{2p_x}^*$ molecular orbitals by overlap of $2p_x$ atomic orbitals on two atoms.

head-on overlap of $2p_x$ orbitals on the two atoms. If the remaining p orbitals overlap (p_y with p_y and p_z with p_z), they must do so sideways, or *side-on*, forming **pi (π) molecular orbitals**. Depending on whether all p orbitals overlap, there can be as many as two π_p and two π_p^* orbitals. Figure 9-4 illustrates the overlap of two corresponding p orbitals on two atoms to form π_p and π_p^* molecular orbitals. There is a nodal plane along the internuclear axis for all pi molecular orbitals. If one views a sigma molecular orbital along the internuclear axis, it appears to be symmetrical around the axis like a pure s atomic orbital. A similar cross-sectional view of a pi molecular orbital looks like a pure p atomic orbital, with a node along the internuclear axis.

► This would involve rotating Figures 9-2, 9-3, and 9-4 by 90° so that the internuclear axes are perpendicular to the plane of the pages.

Unless otherwise noted, all content on this page is © Cengage Learning.

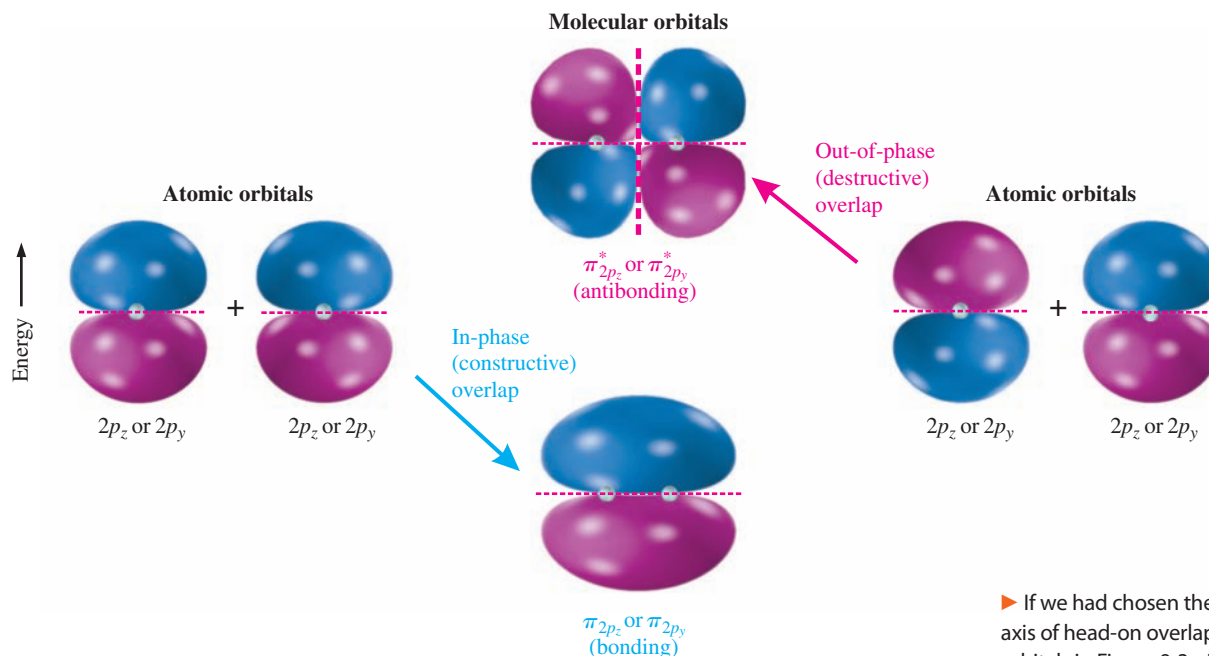


Figure 9-4 The π_{2p} and π_{2p}^* molecular orbitals from overlap of one pair of $2p$ atomic orbitals (for instance, $2p_y$ orbitals). There can be an identical pair of molecular orbitals at right angles to these, formed by another pair of p orbitals on the same two atoms (in this case, $2p_z$ orbitals).

► If we had chosen the z axis as the axis of head-on overlap of the $2p$ orbitals in Figure 9-3, side-on overlap of the $2p_x-2p_x$ and $2p_y-2p_y$ orbitals would form the π -type molecular orbitals.

The number of molecular orbitals formed is equal to the number of atomic orbitals that are combined. When two atomic orbitals are combined, one of the resulting MOs is at a *lower* energy than the original atomic orbitals; this is a *bonding* orbital. The other MO is at a *higher* energy than the original atomic orbitals; this is an *antibonding* orbital.

9-2 Molecular Orbital Energy Level Diagrams

A molecular orbital energy level diagram (MO diagram for short) shows the MOs resulting from combination of the valence atomic orbitals of all atoms of the molecule, arranged in order of increasing energy. Figure 9-5 shows molecular orbital energy level diagrams for homonuclear diatomic molecules of elements in the first and second periods. Each diagram is an extension of the right-hand diagram in Figure 9-2, to which we have added the molecular orbitals formed from $2s$ and $2p$ atomic orbitals.

For the diatomic species shown in Figure 9-5a, the two π_{2p} orbitals are lower in energy than the σ_{2p} orbital. Molecular orbital calculations indicate, however, that for O_2 , F_2 , and hypothetical Ne_2 molecules, the σ_{2p} orbital is lower in energy than the π_{2p} orbitals (see Figure 9-5b).

Diagrams such as these are used to describe the bonding in a molecule in MO terms. Electrons occupy MOs according to the same rules developed for atomic orbitals; they follow the Aufbau Principle, the Pauli Exclusion Principle, and Hund's Rule (see Section 4-18). To obtain the molecular orbital description of the bonding in a molecule or ion, follow these steps:

1. Select (or draw) the appropriate molecular orbital energy level diagram.
2. Determine the *total* number of electrons in the molecule or ion. Note that in applying MO theory, we will account for *all* electrons. This includes both the inner-shell electrons and the valence electrons.

► "Homomuclear" means consisting only of atoms of the same element. "Diatomic" means consisting of two atoms.

► Spectroscopic data support these orders.

► Remember that paramagnetism is an indication that unpaired electrons are present.

3. Distribute the electrons by putting each into the lowest energy level available (Aufbau Principle).
 - a. A maximum of *two* electrons can occupy any given molecular orbital, and then only if they have opposite spin (Pauli Exclusion Principle).
 - b. Electrons must occupy all the orbitals of the same energy singly before pairing begins. These unpaired electrons must have parallel spins (Hund's Rule).

For isolated atoms, we represent the resulting arrangement of electrons in the atomic orbitals as the electron configuration of the atom (e.g., $1s^2 2s^2$). In the same way, we can represent the arrangement of electrons in the molecular orbitals as the electron configuration of the molecule or ion (e.g., $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2}$).

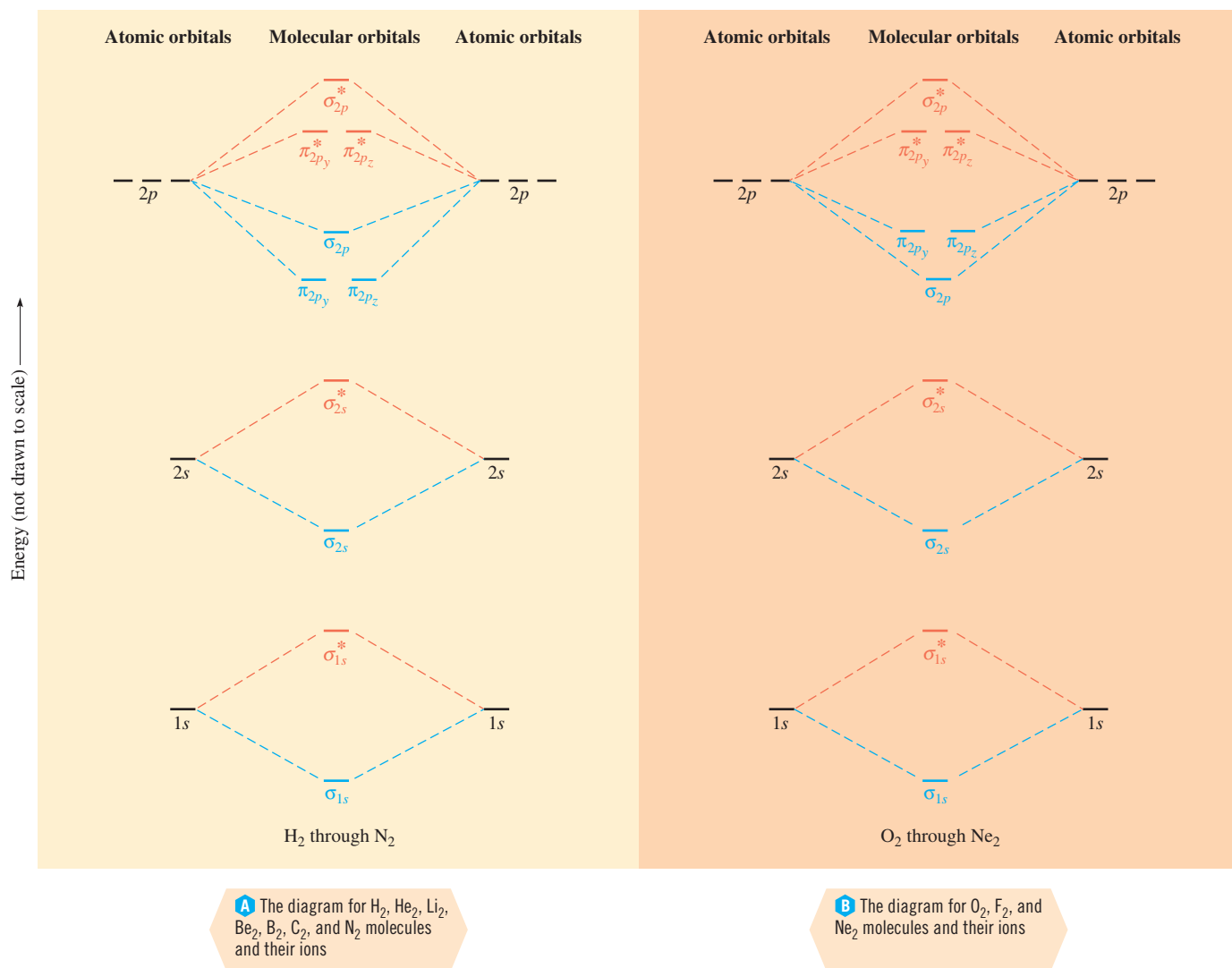


Figure 9-5 Energy level diagrams for first- and second-period homonuclear diatomic molecules and ions (not drawn to scale). The solid lines represent the relative energies of the indicated atomic and molecular orbitals.

9-3 Bond Order and Bond Stability

Now we need a way to judge the stability of a molecule or ion once its energy level diagram has been filled with the appropriate number of electrons. This criterion is the **bond order**:

$$\text{bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of antibonding electrons})}{2}$$

► Electrons in bonding orbitals are often called **bonding electrons**, and electrons in antibonding orbitals are called **antibonding electrons**.

The bond order usually corresponds to the number of bonds described by the valence bond theory. Fractional bond orders exist in species that contain an odd number of electrons, such as the nitrogen oxide molecule, NO (15 electrons), and the superoxide ion, O_2^- (17 electrons).

A bond order *equal to zero* means that the molecule has equal numbers of electrons in bonding MOs (more stable than in separate atoms) and in antibonding MOs (less stable than in separate atoms). Such a molecule would be no more stable than separate atoms, so it would not exist. A bond order *greater than zero* means that more electrons occupy bonding MOs (stabilizing) than antibonding MOs (destabilizing). Such a molecule would be more stable than the separate atoms, and we predict that its existence is possible. But such a molecule could still be quite reactive.

The greater the bond order of a diatomic molecule or ion, the more stable we predict it to be. Likewise, for a bond between two given atoms, the greater the bond order, the shorter is the bond length and the greater is the bond energy.

The **bond energy** is the amount of energy necessary to break a mole of bonds (see Section 15-9); therefore, bond energy is a measure of bond strength.

Problem-Solving Tip Working with MO Theory

MO theory is often the best model to predict the bond order, bond stability, or magnetic properties of a molecule or ion. The procedure is as follows:

1. Select (or draw) the appropriate MO energy level diagram.
2. Count the total number of electrons in the molecule or ion.
3. As each electron is placed in an available orbital having the lowest energy, the Pauli Exclusion Principle and Hund's Rule must be followed.
4. Calculate the bond order = $\left(\frac{\text{bonding } e\text{'s} - \text{antibonding } e\text{'s}}{2} \right)$.
5. Use the bond order to evaluate stability.
6. Look for the presence of unpaired electrons to determine if a species is paramagnetic.

9-4 Homonuclear Diatomic Molecules

The electron configurations for the homonuclear diatomic molecules of the first and second periods are shown in Table 9-1 together with their bond orders, bond lengths, and bond energies. You can derive these electron configurations by putting the required numbers of electrons into the appropriate diagram of Figure 9-5. This procedure is illustrated by the following cases.

► This is just like the Aufbau process we used in Chapter 4 to develop the electron configurations of isolated atoms. There we put electrons into the atomic orbitals of isolated atoms; here we put them into the molecular orbitals of a collection of atoms.

Unless otherwise noted, all content on this page is © Cengage Learning.

The Hydrogen Molecule, H₂

The overlap of the 1s orbitals of two hydrogen atoms produces σ_{1s} and σ_{1s}^* molecular orbitals. The two electrons of the molecule occupy the lower energy σ_{1s} orbital (Figure 9-6a).

Because the only two electrons in an H₂ molecule are in a bonding orbital, the bond order is one. We conclude that the H₂ molecule would be stable, and we know it is. The energy associated with two electrons in the H₂ molecule is lower than that associated with the same two electrons in separate 1s atomic orbitals. The lower the energy of a system, the more stable it is.

$$\text{H}_2 \text{ bond order} = \frac{2-0}{2} = 1$$

The Helium Molecule (Hypothetical), He₂

The energy level diagram for He₂ is similar to that for H₂ except that it has two more electrons. These occupy the antibonding σ_{1s}^* orbital (see Figures 9-5a and 9-6b and Table 9-1), giving He₂ a bond order of zero. That is, the two electrons in the bonding orbital of He₂ would make the molecule *more stable* than the separate atoms. But the two electrons in the antibonding orbital would make the molecule *less stable* than the separate atoms. These effects cancel, so the molecule would be no more stable than the separate atoms. The bond order is zero, and the molecule would not exist. In fact, He₂ is unknown.

$$\text{He}_2 \text{ bond order} = \frac{2-2}{2} = 0$$

The Boron Molecule, B₂

The boron atom has the configuration $1s^2 2s^2 2p^1$. Here p electrons participate in the bonding. Figure 9-5a and Table 9-1 show that the π_{p_y} and π_{p_z} molecular orbitals are lower in energy than the σ_{2p} for B₂. Thus, the electron configuration is

$$\text{B}_2 \text{ bond order} = \frac{6-4}{2} = 1$$

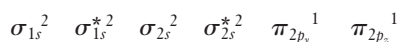


Table 9-1 Molecular Orbitals for First- and Second-Period (Row) Diatomic Molecules^a

	H ₂	He ₂ ^c	Li ₂ ^b	Be ₂ ^c	B ₂ ^b	C ₂ ^b	N ₂	O ₂	F ₂	Ne ₂ ^c
Increasing energy (not to scale)										
σ_{2p}^*	—	—	—	—	—	—	—	—	—	↑↓
$\pi_{2p_y}^*, \pi_{2p_z}^*$	—	—	—	—	—	—	—	↑ ↑ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓
σ_{2p}	—	—	—	—	—	—	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓
π_{2p_y}, π_{2p_z}	—	—	—	—	↑ ↑	↑↓ ↑↓	↑↓ ↑↓	↑↓	↑↓	↑↓
σ_{2s}^*	—	—	—	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
σ_{2s}	—	—	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
σ_{1s}^*	—	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
σ_{1s}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
Paramagnetic?	no	no	no	no	yes	no	no	yes	no	no
Bond order	1	0	1	0	1	2	3	2	1	0
Observed bond length (Å)	0.74	—	2.67	—	1.59	1.31	1.09	1.21	1.43	—
Observed bond energy (kJ/mol)	436	—	110	9	≈ 270	602	945	498	155	—

^aElectron distribution in molecular orbitals, bond order, bond length, and bond energy of homonuclear diatomic molecules of the first- and second-period elements. Note that nitrogen molecules, N₂, have the highest bond energies listed; they have a bond order of three. The species C₂ and O₂, with a bond order of two, have the next highest bond energies.

^bExists only in the vapor state at elevated temperatures.

^cUnknown species.

Unless otherwise noted, all content on this page is © Cengage Learning.

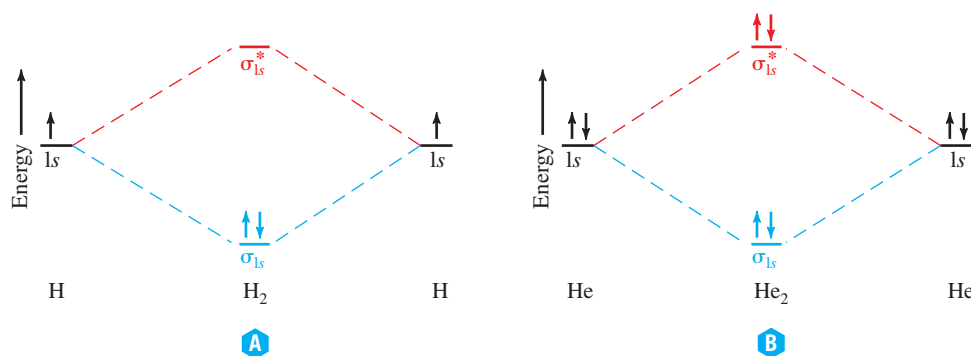


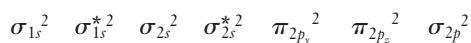
Figure 9-6 Molecular orbital diagrams for (a) H_2 and (b) He_2 .

The unpaired electrons are consistent with the observed paramagnetism of B_2 . Here we illustrate Hund's Rule in molecular orbital theory. The π_{2p_y} and π_{2p_z} orbitals are equal in energy and contain a total of two electrons. Accordingly, one electron occupies each orbital. The bond order is one. Experiments verify that B_2 molecules exist in the vapor state.

► Orbitals of equal energy are called **degenerate orbitals**. Hund's Rule for filling degenerate orbitals was discussed in Section 4-18.

The Nitrogen Molecule, N_2

Experimental thermodynamic data show that the N_2 molecule is stable, is diamagnetic, and has a very high bond energy, 946 kJ/mol. This is consistent with molecular orbital theory. Each nitrogen atom has 7 electrons, so the diamagnetic N_2 molecule has 14 electrons.



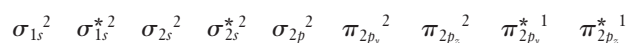
Six more electrons occur in bonding orbitals than in antibonding orbitals, so the bond order is three. We see (Table 9-1) that N_2 has a very short bond length, only 1.09 Å, the shortest of any diatomic species except H_2 .

► N_2 bond order = $\frac{10-4}{2} = 3$

► In the valence bond representation, N_2 is shown as $\text{:N} \equiv \text{N:}$, with a triple bond.

The Oxygen Molecule, O_2

Among the homonuclear diatomic molecules, only N_2 and the very small H_2 have shorter bond lengths than O_2 , 1.21 Å. Recall that valence bond (VB) theory predicts that O_2 is diamagnetic. Experiments show, however, that it is paramagnetic, with two unpaired electrons. MO theory predicts a structure consistent with this observation. For O_2 , the σ_{2p} orbital is lower in energy than the π_{2p_y} and π_{2p_z} orbitals. Each oxygen atom has 8 electrons, so the O_2 molecule has 16 electrons.



The two unpaired electrons reside in the *degenerate* antibonding orbitals, $\pi_{2p_y}^*$ and $\pi_{2p_z}^*$. Because there are four more electrons in bonding orbitals than in antibonding orbitals, the bond order is two (see Figure 9-5b and Table 9-1). We see why the molecule is much more stable than two free O atoms.

► O_2 bond order = $\frac{10-6}{2} = 2$

Similarly, MO theory can be used to predict the structures and stabilities of ions, as Example 9-1 shows.

EXAMPLE 9-1 Predicting Stabilities and Bond Orders

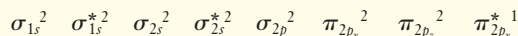
Predict the stabilities and bond orders of the ions (a) O_2^+ and (b) O_2^- .

Plan

- The O_2^+ ion is formed by removing one electron from the O_2 molecule. The electrons that are withdrawn most easily are those in the highest energy orbitals.
- The superoxide ion, O_2^- , results from adding an electron to the O_2 molecule.

Solution

- (a) We remove one of the π_{2p}^* electrons of O_2 to find the configuration of O_2^+ :

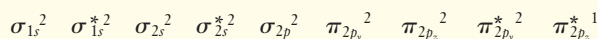


There are five more electrons in bonding orbitals than in antibonding orbitals, so the bond order is 2.5. We conclude that the ion would be reasonably stable, and it does exist.

In fact, the unusual ionic compound $[O_2^+][PtF_6^-]$ played an important role in the discovery of the first noble gas compound, $XePtF_6$ (see Section 28-2).

- (b) We add one electron to the appropriate orbital of O_2 to find the configuration of O_2^- .

Following Hund's Rule, we add this electron into the $\pi_{2p_y}^*$ orbital to form a pair:



There are three more bonding electrons than antibonding electrons, so the bond order is 1.5. We conclude that the ion should exist but be less stable than O_2 .

The known superoxides of the heavier Group 1A elements— KO_2 , RbO_2 , and CsO_2 —contain the superoxide ion, O_2^- . These compounds are formed by combination of the free metals with oxygen (see Section 5-9, second subsection).

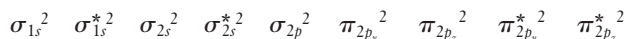
You should now work Exercises 20 and 22.

STOP & THINK

Remember the steps for assessing the stability of a molecule or ion. First, determine the configuration of electrons in its molecular orbitals, as outlined in Section 9-1. Then find the bond order as shown above. The higher the bond order, the more stable we expect the molecule or ion to be.

The Fluorine Molecule, F_2

Each fluorine atom has 9 electrons, so there are 18 electrons in F_2 .



The bond order is one. As you know, F_2 exists. The $F-F$ bond distance is longer (1.43 Å) than the bond distances in O_2 (1.21 Å) or N_2 (1.09 Å) molecules. The bond order in F_2 (one) is less than that in O_2 (two) or N_2 (three). The bond energy of the F_2 molecules is lower than that of either O_2 or N_2 (see Table 9-1). As a result, F_2 molecules are the most reactive of the three.

$$\text{F}_2 \text{ bond order} = \frac{10-8}{2} = 1$$

Heavier Homonuclear Diatomic Molecules

It might appear reasonable to use the same types of molecular orbital diagrams to predict the stability or existence of homonuclear diatomic molecules of the third and subsequent periods. However, the heavier halogens, Cl_2 , Br_2 , and I_2 , which contain only sigma (single) bonds, are the only well-characterized examples at room temperature. We would predict from both molecular orbital theory and valence bond theory that the other (nonhalogen) homonuclear diatomic molecules from below the second period would exhibit pi bonding and therefore multiple bonding.

Some heavier elements, such as S_2 , exist as diatomic species in the vapor phase at elevated temperatures. These species are neither common nor very stable. The instability is related to the inability of atoms of the heavier elements to form strong pi bonds *with each other*. For larger atoms, the sigma bond length is too great to allow the atomic p orbitals on different atoms to overlap very effectively. The strength of pi bonding therefore decreases rapidly with increasing atomic size. For example, N_2 is *much* more stable than P_2 . This is because the $3p$ orbitals on one P atom do not overlap side by side in a pi-bonding manner with corresponding $3p$ orbitals on another P atom nearly as effectively as do the corresponding $2p$ orbitals on the smaller N atoms. MO

theory does not predict multiple bonding for Cl_2 , Br_2 , or I_2 , each of which has a bond order of one.

9-5 Heteronuclear Diatomic Molecules

Heteronuclear Diatomic Molecules of Second-Period Elements

Corresponding atomic orbitals of two different elements, such as the $2s$ orbitals of nitrogen and oxygen atoms, have different energies because their nuclei have different charges and therefore different attractions for electrons. Atomic orbitals of the *more electronegative element* are *lower* in energy than the corresponding orbitals of the less electronegative element. Accordingly, a molecular orbital diagram such as Figure 9-5 is inappropriate for *heteronuclear* diatomic molecules. If the two elements are similar (as in NO or CN molecules, for example), we can modify the diagram of Figure 9-5 by skewing it slightly. Figure 9-7 shows the energy level diagram and electron configuration for nitrogen oxide, NO, also known as nitric oxide.

► *Note:* CN is a reactive molecule, not the stable cyanide ion, CN^- .

The closer the energy of a molecular orbital is to the energy of one of the atomic orbitals from which it is formed, the more of the character of that atomic orbital it shows. Thus, as we see in Figure 9-7, the bonding MOs in the NO molecule have more oxygen-like atomic orbital character, and the antibonding orbitals have more nitrogen-like atomic orbital character.

In general the energy differences ΔE_1 , ΔE_2 , and ΔE_3 (orange backgrounds in Figure 9-7) depend on the difference in electronegativities between the two atoms. The greater these energy differences, the more polar is the bond joining the atoms and the greater is its ionic character. On the other hand, the energy differences reflect the degree of overlap between

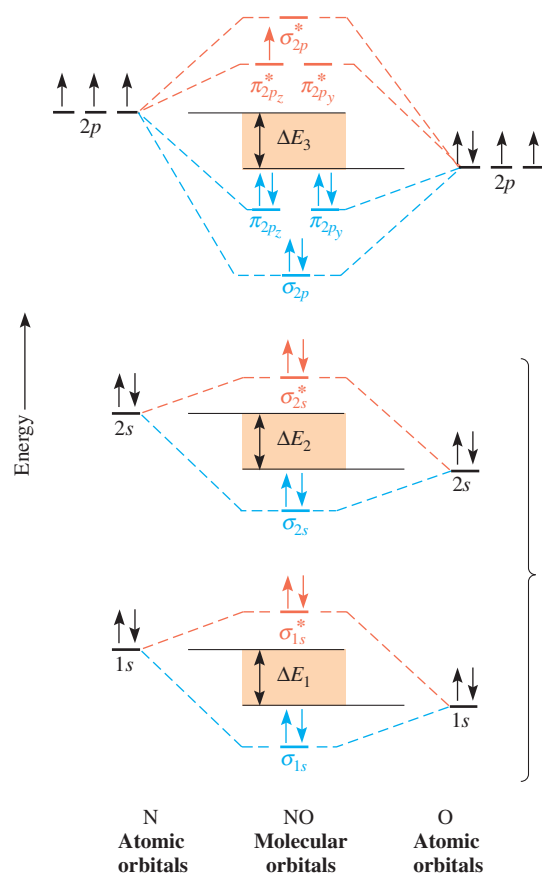


Figure 9-7 MO energy level diagram for nitrogen oxide, NO, a slightly polar heteronuclear diatomic molecule ($\mu = 0.15 \text{ D}$). The atomic orbitals of oxygen, the more electronegative element, are a little lower in energy than the corresponding atomic orbitals of nitrogen, the less electronegative element. For this molecule, the energy differences ΔE_1 , ΔE_2 , and ΔE_3 are not very large; the molecule is not very polar.

Unless otherwise noted, all content on this page is © Cengage Learning.

atomic orbitals; the smaller these differences are, the more the orbitals can overlap, and the greater the covalent character of the bond is.

We see that NO has a total of 15 electrons, making it isoelectronic with the N_2^- ion. The distribution of electrons is therefore the same in NO as in N_2^- , although we expect the energy levels of the MOs to be different. In accord with our predictions, nitrogen oxide is a stable molecule. It has a bond order of 2.5, a short nitrogen–oxygen bond length of 1.15 Å, a low dipole moment of 0.15 D, and a high bond energy of 891 kJ/mol.

The Hydrogen Fluoride Molecule, HF

The electronegativity difference between hydrogen (EN = 2.1) and fluorine (EN = 4.0) is very large [$\Delta(\text{EN}) = 1.9$]. The hydrogen fluoride molecule contains a very polar bond ($\mu = 1.91$ D). The bond in HF involves the $1s$ electron of H and an unpaired electron from a $2p$ orbital of F. Figure 9-8 shows the overlap of the $1s$ orbital of H with a $2p$ orbital of F to form σ_{sp} and σ_{sp}^* molecular orbitals. The remaining two $2p$ orbitals of F have no net overlap with H orbitals. They are called **nonbonding molecular orbitals**. The same is true for the F $2s$ and $1s$ orbitals. These nonbonding orbitals retain the characteristics of the F atomic orbitals from which they are formed. The MO diagram of HF is shown in Figure 9-9.

Other Diatomic Species with Large $\Delta(\text{EN})$ Values

If the energies of the atomic orbitals of the two atoms of a diatomic molecule or ion are quite different, the MO diagram may be unlike that known for any homonuclear species. Its unique MO diagram is constructed by combining the Schrödinger equations for the two atoms. Construction of the MO diagram for CO is a complex case, beyond the coverage in this textbook.

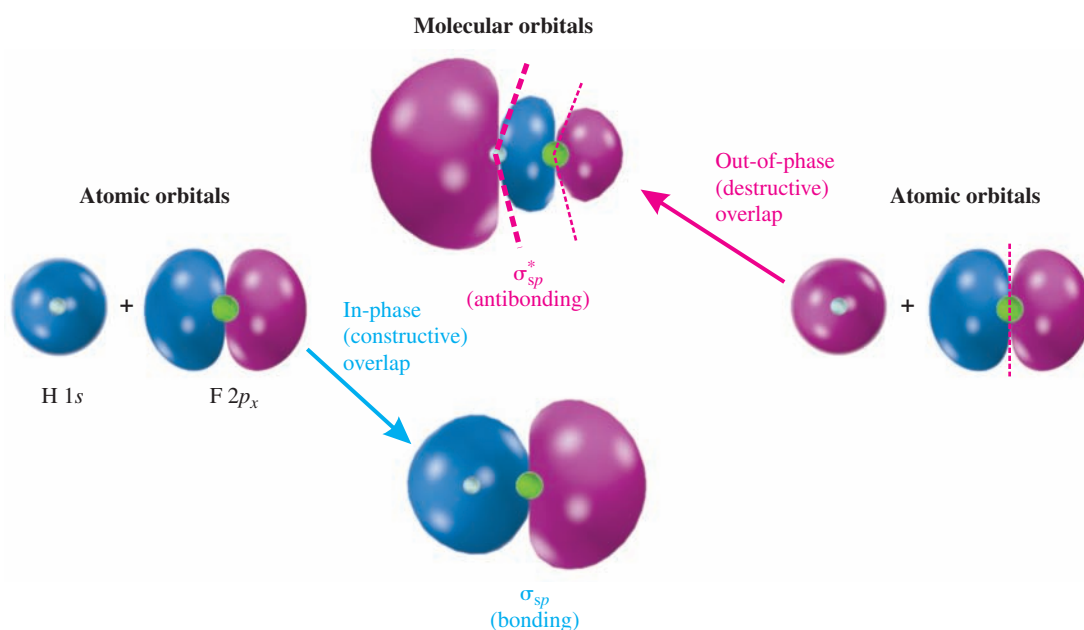


Figure 9-8 Formation of σ_{sp} and σ_{sp}^* molecular orbitals in HF by overlap of the $1s$ orbital of H with a $2p$ orbital of F.

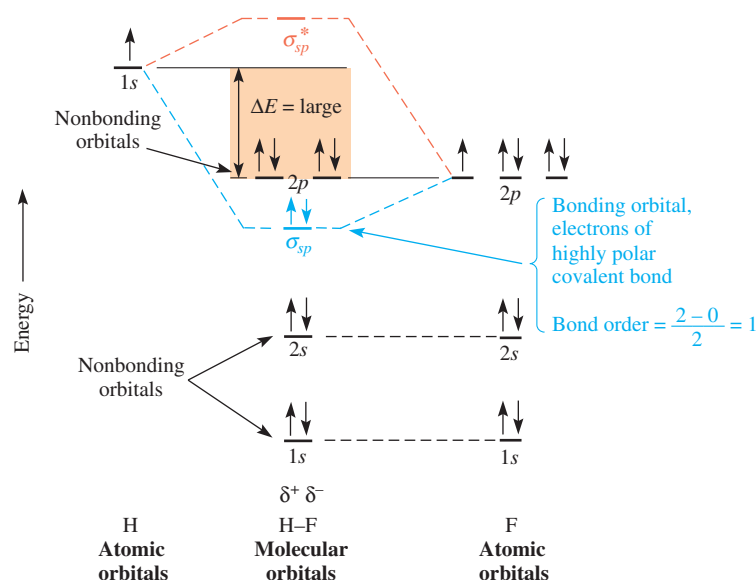


Figure 9-9 MO energy level diagram for hydrogen fluoride, HF, a very polar molecule ($\mu = 1.91$ D). ΔE is large because the electronegativity difference is large.

9-6 Delocalization and the Shapes of Molecular Orbitals

In Section 7-9 we described resonance formulas for molecules and polyatomic ions. Resonance is said to exist when two or more equivalent Lewis formulas can be written for the same species and a single such formula does not account for the properties of a substance. In molecular orbital terminology, a more appropriate description involves delocalization of electrons. The shapes of molecular orbitals for species in which electron **delocalization** occurs can be predicted by combining all the contributing atomic orbitals.

The Carbonate Ion, CO_3^{2-}

Consider the trigonal planar carbonate ion, CO_3^{2-} as an example. All the carbon–oxygen bonds in the ion have the same bond length and the same energy, intermediate between those of typical $\text{C}=\text{O}$ and $\text{C}-\text{O}$ bonds. Valence bond theory describes the ion in terms of three contributing resonance structures (Figure 9-10a). No one of the three resonance forms adequately describes the bonding.

According to valence bond theory, the C atom is described as sp^2 hybridized, and it forms one sigma bond with each of the three O atoms. This leaves one unhybridized $2p$ atomic orbital on the C atom, say the $2p_z$ orbital. This orbital is capable of overlapping and mixing with the $2p_z$ orbital of any of the three O atoms. The sharing of two electrons in the resulting localized pi orbital would form a pi bond. Thus, three equivalent resonance structures can be drawn in valence bond terms (see Figure 9-10b). We emphasize that there is *no evidence* for the existence of these separate resonance structures.

The MO description of the pi bonding involves the simultaneous overlap and mixing of the carbon $2p_z$ orbital with the $2p_z$ orbitals of all three oxygen atoms. This forms a delocalized bonding pi molecular orbital lying above and below the plane of the sigma system, as well as an antibonding pi orbital. The electron pair that occupies this delocalized bonding pi MO is spread over all four atoms, as depicted in Figure 9-10c. The bonding in such species as nitrate ion, NO_3^- , and ozone, O_3 , can be described similarly.

► This section includes pictorial representations of molecular orbitals. The details of the corresponding molecular orbital diagrams are too complicated to present here.

► The average carbon–oxygen bond order in the CO_3^{2-} ion is $1\frac{1}{3}$.

► In a polyatomic molecule or ion, MOs can be formed by overlap of the AOs of more than two atoms.

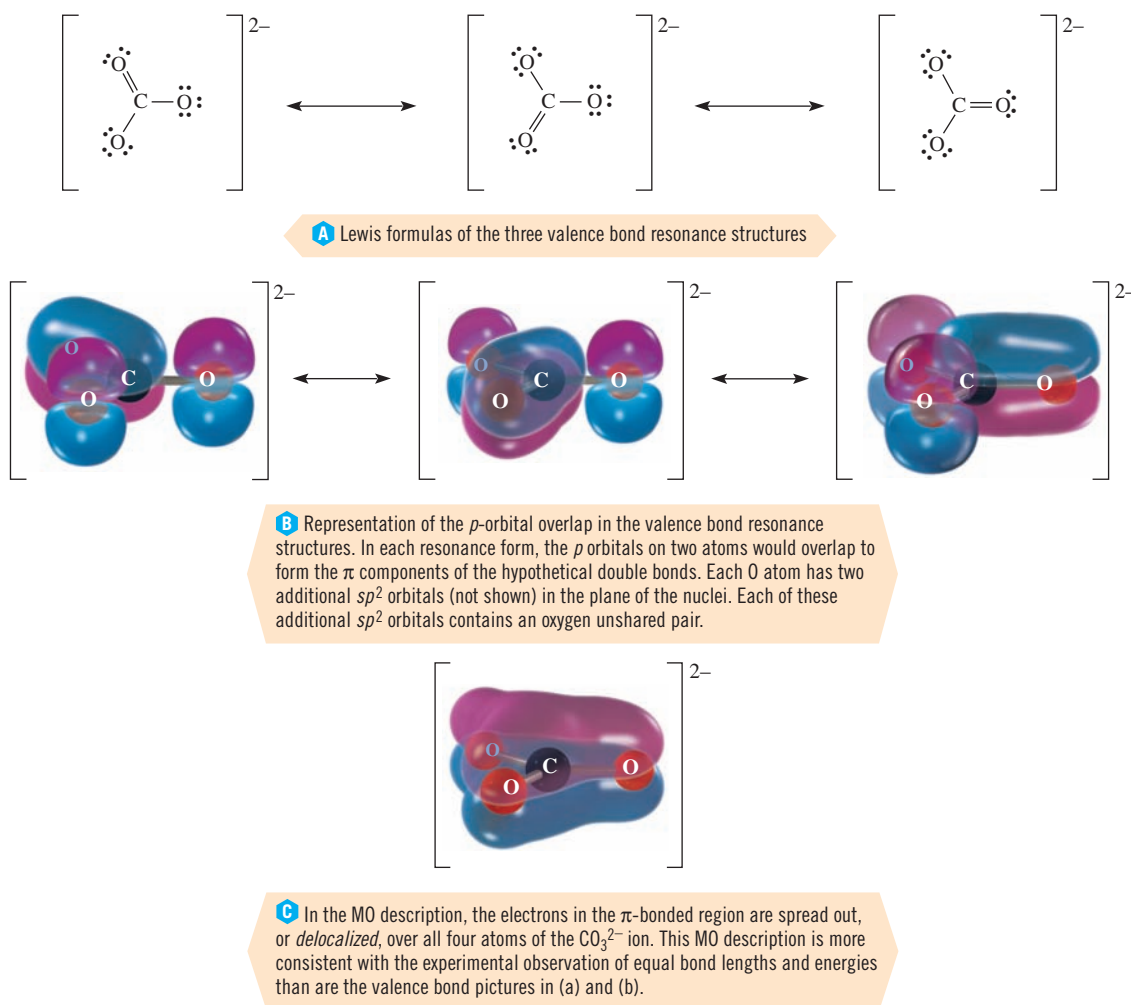


Figure 9-10 Alternative representations of the bonding in the carbonate ion, CO_3^{2-} .

The Benzene Molecule, C_6H_6

► There is no evidence for the existence of either of these forms of benzene. The MO description of benzene is far better than the valence bond description.

Now let us consider the benzene molecule, C_6H_6 , whose two valence bond resonance forms are shown in Figure 9-11a. The valence bond description involves sp^2 hybridization at each C atom. Each C atom is at the center of a trigonal plane, and the entire molecule is known to be planar. There are sigma bonds from each C atom to the two adjacent C atoms and to one H atom. This leaves one unhybridized $2p_z$ orbital on each C atom and one remaining valence electron for each. According to valence bond theory, adjacent pairs of $2p_z$ orbitals and the six remaining electrons occupy the regions of overlap to form a total of three pi bonds in either of the two ways shown in Figure 9-11b.

Experimental studies of the C_6H_6 structure prove that it does *not* contain alternating single and double carbon-carbon bonds. The usual C—C single bond length is 1.54 Å, and the usual C=C double bond length is 1.34 Å. All six of the carbon-carbon bonds in benzene are observed to be the same length, 1.39 Å, intermediate between those of single and double bonds.

This is well explained by the MO theory, which predicts that the six $2p_z$ orbitals of the C atoms overlap and mix to form three pi-bonding and three pi-antibonding molecular orbitals. The delocalized bonding pi molecular orbitals of benzene are shown in Figure 9-11c. The six pi electrons occupy these three bonding MOs. Thus, they are distributed throughout the molecule as a whole, above and below the plane of the sigma-bonded framework. This results in identical character for all carbon-carbon bonds in benzene. The MO representation of the extended pi system is the same as that obtained by averaging the two contributing valence bond resonance structures.

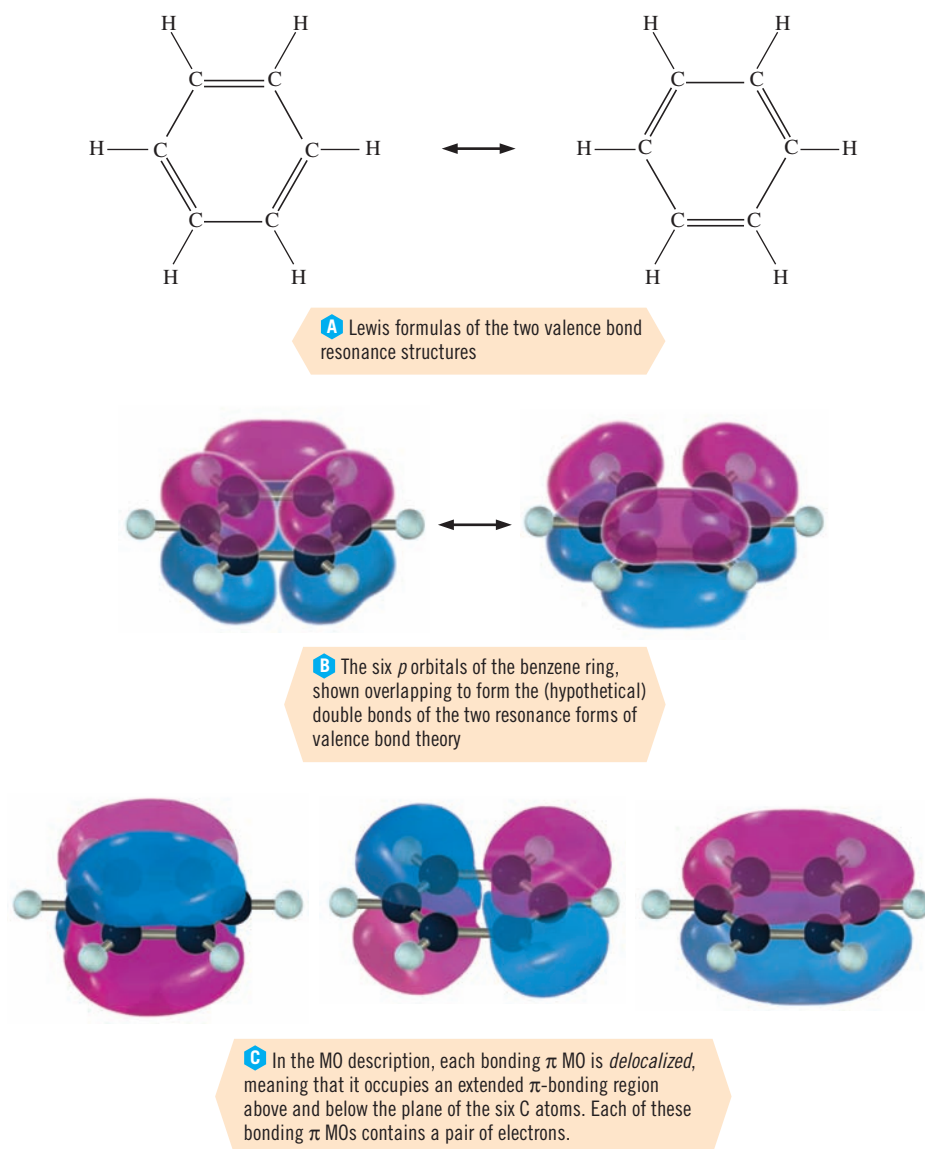


Figure 9-11 Representations of the bonding in the benzene molecule, C_6H_6 .

KEY TERMS

Antibonding electrons Electrons in antibonding orbitals.

Antibonding molecular orbital A molecular orbital higher in energy than any of the atomic orbitals from which it is derived; when populated with electrons, lends instability to a molecule or ion. Denoted with an asterisk (*) superscript on its symbol.

Bond energy The amount of energy necessary to break one mole of bonds of a given kind (in the gas phase).

Bond order Half the number of electrons in bonding orbitals minus half the number of electrons in antibonding orbitals.

Bonding electrons Electrons in bonding orbitals.

Bonding molecular orbital A molecular orbital lower in energy than any of the atomic orbitals from which it is derived; when populated with electrons, lends stability to a molecule or ion.

Degenerate orbitals Orbitals of the same energy.

Delocalization The formation of a set of molecular orbitals that extend over more than two atoms; important in species

that valence bond theory describes in terms of resonance (see Section 7-6).

Heteronuclear Consisting of different elements.

Homonuclear Consisting of only one element.

Molecular orbital (MO) An orbital resulting from overlap and mixing of atomic orbitals on different atoms. An MO belongs to the molecule as a whole.

Molecular orbital theory A theory of chemical bonding based on the postulated existence of molecular orbitals.

Nodal plane A region in which the probability of finding an electron is zero; also known as a *node*.

Nonbonding molecular orbital A molecular orbital derived only from an atomic orbital of one atom; lends neither stability nor instability to a molecule or ion when populated with electrons.

Pi (π) bond A bond resulting from electron occupancy of a pi molecular orbital.

Unless otherwise noted, all content on this page is © Cengage Learning.

Pi (π) molecular orbital A molecular orbital resulting from side-on overlap of atomic orbitals.

Sigma (σ) bond A bond resulting from electron occupancy of a sigma molecular orbital.

Sigma (σ) molecular orbital A molecular orbital resulting from head-on overlap of two atomic orbitals.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

MO Theory: General Concepts

- Describe the main differences between the valence bond theory and the molecular orbital theory.
- In molecular orbital theory, what is a molecular orbital? What two types of information can be obtained from molecular orbital calculations? How do we use such information to describe the bonding within a molecule?
- What is the relationship between the maximum number of electrons that can be accommodated by a set of molecular orbitals and the maximum number that can be accommodated by the atomic orbitals from which the MOs are formed? What is the maximum number of electrons that one MO can hold?
- Answer Exercise 3 after replacing “molecular orbitals” or “MO” with “hybridized atomic orbitals.”
- What differences and similarities exist among (a) atomic orbitals, (b) localized hybridized atomic orbitals according to valence bond theory, and (c) molecular orbitals?
- Describe the shapes, including the locations of the nuclei, of σ and σ^* orbitals.
- Describe the shapes, including the locations of the nuclei, of π and π^* orbitals.
- State the three rules for placing electrons in molecular orbitals.
- What is meant by the term “bond order”? How is the value of the bond order calculated?
- Compare and illustrate the differences between (a) atomic orbitals and molecular orbitals, (b) bonding and antibonding molecular orbitals, (c) σ orbitals and π orbitals, and (d) localized and delocalized molecular orbitals.
- Is it possible for a molecule or polyatomic ion in its ground state to have a negative bond order? Why?
- What is the relationship between the energy of a bonding molecular orbital and the energies of the original atomic orbitals? What is the relationship between the energy of an antibonding molecular orbital and the energies of the original atomic orbitals?
- Compare and contrast the following three concepts: (a) bonding orbitals; (b) antibonding orbitals; (c) nonbonding orbitals.

Homonuclear Diatomic Species

- What do we mean when we say that a molecule or ion is (a) homonuclear, (b) heteronuclear, or (c) diatomic?
- Use the appropriate molecular orbital energy diagram to write the electron configurations of the following molecules and ions: (a) Be_2 , Be_2^+ , Be_2^- ; (b) B_2 , B_2^+ , B_2^- .
- What is the bond order of each of the species in Exercise 15?
- Which of the species in Exercise 15 are diamagnetic and which are paramagnetic? How many unpaired electrons are indicated by the MO description of each species?
- Use MO theory to predict relative stabilities of the species in Exercise 15. Comment on the validity of these predictions. What else *must* be considered in addition to electron occupancy of MOs?
- Use the appropriate molecular orbital energy diagram to write the electron configuration for each of the following; calculate the bond order of each, and predict which would exist. (a) H_2^+ ; (b) H_2 ; (c) H_2^- ; (d) H_2^{2-} .
- Repeat Exercise 19 for (a) Ne_2^+ ; (b) Ne_2 ; (c) Ne_2^{2+} .
- Repeat Exercise 19 for (a) N_2 ; (b) He_2 ; (c) C_2^{2-} .
- Repeat Exercise 19 for (a) Li_2 ; (b) Li_2^+ ; (c) O_2^{2-} .
- ▲ Which homonuclear diatomic molecules or ions of the second period have the following electron distributions in MOs? In other words, identify X in each.
 - $\text{X}_2 \quad \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_y}^2 \pi_{2p_z}^2 \sigma_{2p}^2$
 - $\text{X}_2 \quad \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p_y}^2 \pi_{2p_z}^2 \pi_{2p_y}^{*1} \pi_{2p_z}^{*1}$
 - $\text{X}_2^- \quad \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p_y}^2 \pi_{2p_z}^2 \sigma_{2p}^2 \pi_{2p_y}^{*1}$
- What is the bond order of each of the species in Exercise 23?
- Write MO electron configurations for (a) F_2 , F_2^- , F_2^+ ; (b) C_2 , C_2^+ , C_2^- .
- (a) What is the bond order of each species in Exercise 25? (b) Are they diamagnetic or paramagnetic? (c) What would MO theory predict about the stabilities of these species?
- (a) Give the MO designations for O_2 , O_2^- , O_2^{2-} , O_2^+ , and O_2^{2+} . (b) Give the bond order in each case. (c) Match these species with the following observed bond lengths: 1.04 Å, 1.12 Å, 1.21 Å, 1.33 Å, and 1.49 Å.
- (a) Give the MO designations for N_2 , N_2^- , and N_2^+ . (b) Give the bond order in each case. (c) Rank these three species by increasing predicted bond length.

● **Molecular Reasoning** exercises

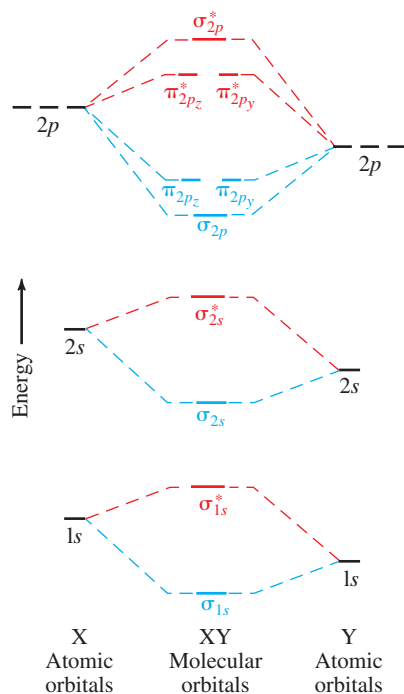
▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

Heteronuclear Diatomic Species

The following is a molecular orbital energy level diagram for a heteronuclear diatomic molecule, XY, in which both X and Y are from Period 2 and Y is slightly more electronegative. This diagram may be used in answering questions in this section.



29. Use the preceding diagram to fill in an MO diagram for NO^- . What is the bond order of NO^- ? Is it paramagnetic? How would you assess its stability?
30. Repeat Exercise 29 for NO^+ .
31. Repeat Exercise 29 for CN^- . Refer to the preceding diagram, but assume that the π_{2p_y} and π_{2p_z} MOs are lower in energy than the σ_{2p} MO.
32. Compare the MO descriptions for CN , CN^+ , CN^{2+} , CN^- , and CN^{2-} . Refer to the preceding diagram but assume that the π_{2p_y} and π_{2p_z} MOs are lower in energy than the σ_{2p} MO. Which would be most stable? Which would you predict to be paramagnetic? Why? Determine the bond order of each.
33. Oxygen, O_2 , can acquire one or two electrons to give O_2^- (superoxide ion) or O_2^{2-} (peroxide ion). Write the electron configuration for the ions in molecular orbital terms, and then compare them with the O_2 molecule on the following bases. (a) magnetic character; (b) net number of σ and π bonds; (c) bond order; (d) oxygen–oxygen bond length.
34. For each of the two species NF and NF^+ , (a) draw MO energy level diagrams; (b) write out electron configurations; (c) determine bond orders and predict relative stabilities; and (d) predict diamagnetism or paramagnetism.
35. The nitrosyl ion, NO^+ , has an interesting chemistry.
 - (a) Is NO^+ diamagnetic or paramagnetic? If paramagnetic, how many unpaired electrons does it have?

- (b) Assume the molecular orbital diagram for a homonuclear diatomic molecule (see Figure 9-5a) applies to NO^+ . What is the highest-energy molecular orbital occupied by electrons?
 - (c) What is the nitrogen–oxygen bond order?
 - (d) Is the $\text{N}—\text{O}$ bond in NO^+ stronger or weaker than the bond in NO ?
36. To decrease the strength of the bonding in the hypothetical compound BC , would you add or subtract an electron? Explain your answer with the aid of an MO electron structure.

Delocalization

37. Use Lewis formulas to depict the resonance structures of the following species from the valence bond point of view, and then sketch MOs for the delocalized π systems: (a) NO_3^- , nitrate ion; (b) HCO_3^- , hydrogen carbonate ion (H is bonded to O); (c) NO_2^- , nitrite ion.
38. Use Lewis formulas to depict the resonance structures of the following species from the valence bond point of view, and then sketch MOs for the delocalized π systems: (a) SO_2 , sulfur dioxide; (b) O_3 , ozone; (c) HCO_2^- , formate ion (H is bonded to C).

Mixed Exercises

39. Draw and label the complete MO energy level diagrams for the following species. For each, determine the bond order, predict the stability of the species, and predict whether the species will be paramagnetic or diamagnetic. (a) He_2^+ ; (b) CN ; (c) HeH^+ .



A paramagnetic material is attracted toward a magnetic field.

40. Draw and label the complete MO energy level diagrams for the following species. For each, determine the bond order, predict the stability of the species, and predict whether the species will be paramagnetic or diamagnetic. (a) O_2^{2+} ; (b) HO^- ; (c) HF .
41. Which of these species would you expect to be paramagnetic and which to be diamagnetic? (a) He_2^- ; (b) N_2 ; (c) NO^+ ; (d) N_2^{2+} ; (e) F_2^+ .

Conceptual Exercises

42. ● Refer to the diagrams in Figure 9-5 as needed.
 (a) Can the bond order of a diatomic species having 20 or fewer electrons be greater than three? Why? (b) Can the bond order be a value that is not divisible by 0.5? Why?
43. ● As NO ionizes to form NO^+ , does the nitrogen–oxygen bond become stronger or weaker?



44. Which of the homonuclear diatomic molecules of the second row of the periodic table (Li_2 to Ne_2) are predicted by MO theory to be paramagnetic? Which ones are predicted to have a bond order of one? Which ones are predicted to have a bond order of two? Which one is predicted to have the highest bond order?
45. ●▲ Use valence bond and molecular orbital theory to describe the change in $\text{Cl}-\text{Cl}$ bond length when Cl_2 loses an electron to form Cl_2^+ . Would the cation be diamagnetic or paramagnetic? Explain.
46. ●▲ Briefly explain the finding that the $\text{N}-\text{O}$ bond is longer in NO^- than in NO . Should NO^- exist? If so, how would its bond length compare with those in NO^+ and NO ? What is the bond order of each species?
47. The validity of molecular orbital theory is supported by its ability, unlike valence bond theory, to correctly predict certain properties of homonuclear diatomic molecules of elements in the first and second periods. What prediction would valence bond theory make about the paramagnetism of these molecules? For which molecules does molecular orbital theory make a different prediction?
48. For which of the molecules in Exercise 47 does molecular orbital theory allow us to make a prediction about the bond order that we might not make on the basis of valence bond theory? Describe the level of agreement between the bond order predicted by molecular orbital theory and the observed bond length and bond energy. (Also consider the atomic radii.)
49. ●▲ For which of the homonuclear diatomic molecules or ions of elements in the first and second periods would the paramagnetism or the bond order actually be different if the incorrect energy level diagram (Figure 9-5a vs. Figure 9-5b) were used? (*Hint*: There are four or more correct answers.)

50. What effect does the addition of electrons to a bonding orbital have on the bond strength? What effect does the addition of electrons to an antibonding orbital have on the bond strength? What effect does the addition of electrons to a nonbonding orbital have on the bond strength?

Building Your Knowledge

51. ● When carbon vaporizes at extremely high temperatures, the diatomic molecule C_2 is among the species present in the vapor. Write a Lewis formula for C_2 . Does your Lewis formula of C_2 obey the octet rule? (C_2 does not contain a quadruple bond.) Does C_2 contain a single, a double, or a triple bond? Is it paramagnetic or diamagnetic? Show how molecular orbital theory can be used to predict the answers to questions left unanswered by valence bond theory.
52. ●▲ Rationalize the following observations in terms of the stabilities of σ and π bonds. (a) The most common form of nitrogen is N_2 , whereas the most common form of phosphorus is P_4 (see the structure in Figure 1-4). (b) The most common forms of oxygen are O_2 and (less common) O_3 , whereas the most common form of sulfur is S_8 .

Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

53. Use an internet search engine (such as <http://www.google.com>) to locate information on vision and molecular orbital theory. How are the two related?
54. ▲ Use an internet search engine (such as <http://www.google.com>) to locate information on the comparison of other bonding theories (such as valence bond theory, crystal field theory, band theory, and metallic bonding) to molecular orbital theory. How are they related?
55. Open www.winter.group.shef.ac.uk/orbitron or another suitable animated discussion of Molecular Orbital Theory. (a) Click on π_x and watch the animation. Describe the final product shown. (b) Click on π_x^* and watch the animation. Describe the final product shown.

Reactions in Aqueous Solutions I: Acids, Bases, and Salts

10



The acid-base reaction of citric acid and sodium bicarbonate (NaHCO_3) when placed into water produces carbon dioxide (CO_2) bubbles and the fizz in an Alka Seltzer™ tablet.

Charles D. Winters

OUTLINE

- 10-1 Properties of Aqueous Solutions of Acids and Bases
- 10-2 The Arrhenius Theory
- 10-3 The Hydronium Ion (Hydrated Hydrogen Ion)
- 10-4 The Brønsted–Lowry Theory
- 10-5 The Autoionization of Water
- 10-6 Amphoterism
- 10-7 Strengths of Acids
- 10-8 Acid–Base Reactions in Aqueous Solutions
- 10-9 Acidic Salts and Basic Salts
- 10-10 The Lewis Theory
- 10-11 The Preparation of Acids

Unless otherwise noted, all content on this page is © Cengage Learning.

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Describe the Arrhenius theory of acids and bases
- ▶ Describe hydrated hydrogen ions
- ▶ Describe the Brønsted–Lowry theory of acids and bases
- ▶ List properties of aqueous solutions of acids
- ▶ List properties of aqueous solutions of bases
- ▶ Arrange binary acids in order of increasing strength
- ▶ Arrange ternary acids in order of increasing strength
- ▶ Describe the Lewis theory of acids and bases
- ▶ Complete and balance equations for acid–base reactions
- ▶ Define acidic and basic salts
- ▶ Explain amphoterism
- ▶ Describe methods for preparing acids

In technological societies, acids, bases, and salts are indispensable compounds. Table 6-10 lists the 14 such compounds that were included in the top 50 chemicals produced in the United States in 2009. The production of sulfuric acid (H_2SO_4 , number 1) was more than three times as great as the production of ammonia (NH_3). Sixty-five percent of the H_2SO_4 is used in the production of fertilizers.

Many acids, bases, and salts occur in nature and serve a wide variety of purposes. For instance, your stomach “digestive juice” contains approximately 0.10 mole of hydrochloric acid (HCl) per liter. Human blood and the aqueous components of most cells are slightly basic. The liquid in your car battery is approximately 40% H_2SO_4 by mass. Baking soda (NaHCO_3) is a salt of carbonic acid (H_2CO_3). Sodium hydroxide (NaOH), a base, is used in the manufacture of soaps, paper, and many other chemicals. “Drano” is solid NaOH that contains some aluminum chips. Sodium chloride (NaCl) is used to season food and as a food preservative. Calcium chloride (CaCl_2) is used to melt ice on highways and in the emergency treatment of cardiac arrest. Several ammonium salts are used as fertilizers. Many organic acids (carboxylic acids) and their derivatives occur in nature. Acetic acid is present in vinegar; the sting of an ant bite is due to formic acid. Amino acids are carboxylic acids that also contain basic groups derived from ammonia. Amino acids are the building blocks of proteins, which are important materials in all forms of life. The pleasant odors and flavors of ripe fruit are due in large part to the presence of esters (see Chapter 23) that are formed from organic acids in unripe fruit.

▶ You will encounter many of these in your laboratory work.



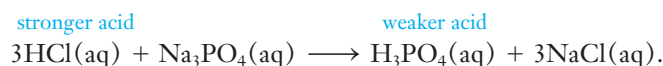
(Left) Many common household liquids are acidic, including soft drinks, vinegar, and fruit juices. (Right) Most cleaning materials are basic.

10-1 Properties of Aqueous Solutions of Acids and Bases

Aqueous solutions of most **protic acids** (those containing acidic hydrogen atoms) exhibit certain properties, which are properties of hydrated hydrogen ions in aqueous solution.

► Chemists also use “protonic” to describe these acids.

1. Acids have a sour taste. Pickles are usually preserved in vinegar, a 5% solution of acetic acid. Many pickled condiments contain large amounts of sugar so that the taste of acetic acid is partially masked by the sweet taste of sugar. Lemons contain citric acid, which is responsible for their characteristic sour taste.
2. Acids change the colors of many indicators (highly colored dyes whose colors depend on the acidic or basic character of the solution). Acids turn blue litmus red, and cause bromthymol blue to change from blue to yellow.
3. Nonoxidizing acids react with metals above hydrogen in the activity series (see Section 6-8, Part 2) to liberate hydrogen gas, H_2 . (Nitric acid, HNO_3 , a common oxidizing acid, reacts with metals to produce primarily nitrogen oxides.)
4. Acids react with (neutralize) metal oxides and metal hydroxides to form salts and water (see Section 6-8, Part 1).
5. Acids react with salts of weaker acids to form the weaker acid and the salt of the stronger acid; for example,



6. Aqueous solutions of acids conduct an electric current because they are totally or partially ionized.

Aqueous solutions of most bases also exhibit certain properties, which are due to the hydrated hydroxide ions present in aqueous solutions of bases.

1. Bases have a bitter taste.
2. Bases have a slippery feeling. Soaps are common examples that are mildly basic. A solution of household bleach feels very slippery because it is quite basic.
3. Bases change the colors of many indicators: bases turn litmus from red to blue, and bromthymol blue changes from yellow to blue.
4. Bases react with (neutralize) acids to form salts and, in most cases, water.
5. Their aqueous solutions conduct an electric current because bases are dissociated or ionized to some extent.

CAUTION!

We should *never* try to identify a substance in the laboratory by taste. You have, however, probably experienced the sour taste of acetic acid in vinegar or citric acid in foods that contain citrus fruits.



The indicator bromthymol blue is yellow in acidic solution and blue in basic solution.

10-2 The Arrhenius Theory

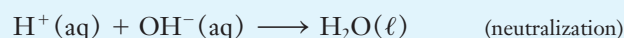
In 1680, Robert Boyle noted that acids (1) dissolve many substances, (2) change the colors of some natural dyes (indicators), and (3) lose their characteristic properties when mixed with alkalis (bases). By 1814, J. Gay-Lussac concluded that acids *neutralize* bases and that the two classes of substances should be defined in terms of their reactions with each other.

In 1884, Svante Arrhenius (1859–1927) presented his theory of electrolytic dissociation, which resulted in the Arrhenius theory of acid–base reactions. In his view,

an **acid** is a substance that contains hydrogen and produces H^+ in aqueous solution.

A **base** is a substance that contains the OH (hydroxyl) group and produces hydroxide ions, OH^- , in aqueous solution.

Neutralization is defined as the reaction of H^+ ions with OH^- ions to form H_2O molecules.

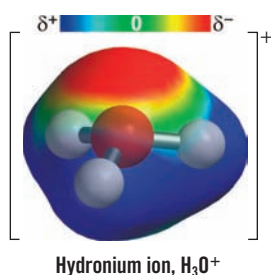


► This is an extremely important concept.

► Review Sections 5-8, 5-9, 6-1, and 6-9 (Part 1).

► The most common isotope of hydrogen, ^1H , has no neutrons. Thus, $^1\text{H}^+$ is a bare proton. In discussions of acids and bases, we use the terms *hydrogen ion*, *proton*, and H^+ interchangeably.

► The actual value of n may be as large as 17, but $n = 4$ is the most commonly accepted value.



► The Brønsted–Lowry theory is especially useful for reactions in aqueous solutions. It is widely used in medicine and in the biological sciences.

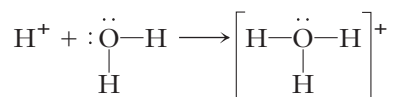
The Arrhenius theory of acid–base behavior satisfactorily explained reactions of *protic acids* with metal hydroxides (hydroxy bases). It was a significant contribution to chemical thought and theory in the latter part of the nineteenth century. The Arrhenius model of acids and bases, although limited in scope, led to the development of more general theories of acid–base behavior. They will be considered in later sections.

10-3 The Hydronium Ion (Hydrated Hydrogen Ion)

Although Arrhenius described H^+ ions in water as bare ions (protons), we now know that they are hydrated in aqueous solution and exist as $\text{H}^+(\text{H}_2\text{O})_n$, in which n is some small integer. This is due to the attraction of the H^+ ions, or protons, for the oxygen end (δ^-) of water molecules. Although we do not know the extent of hydration of H^+ in most solutions, we usually represent the hydrated hydrogen ion as the **hydronium ion**, H_3O^+ , or $\text{H}^+(\text{H}_2\text{O})_n$, in which $n = 1$.

The hydrated hydrogen ion is the species that gives aqueous solutions of acids their characteristic acidic properties.

Whether we use the designation $\text{H}^+(\text{aq})$ or H_3O^+ , we always mean the hydrated hydrogen ion.



10-4 The Brønsted–Lowry Theory

In 1923, J. N. Brønsted (1879–1947) and T. M. Lowry (1874–1936) independently presented logical extensions of the Arrhenius theory. Brønsted's contribution was more thorough than Lowry's, and the result is known as the **Brønsted theory** or the **Brønsted–Lowry theory**.

An **acid** is defined as a *proton donor* (H^+), and a **base** is defined as a *proton acceptor*.

These definitions are sufficiently broad that any hydrogen-containing molecule or ion capable of releasing a proton, H^+ , is an acid, whereas any molecule or ion that can accept a proton is a base. In the Arrhenius theory of acids and bases, only substances that contain the OH^- group would be called bases. The Brønsted–Lowry theory expands the definition of bases to include substances that have one or more lone pairs of electrons that can act as proton acceptors.

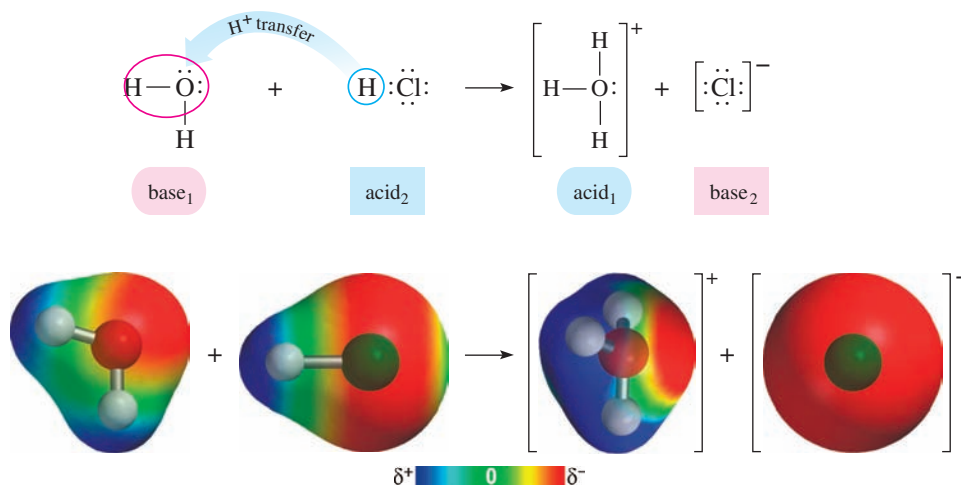
An acid–base reaction is the transfer of a proton from an acid to a base.

Thus, the complete ionization of hydrogen chloride, HCl , a *strong* acid, in water is an acid–base reaction in which water acts as a base or proton acceptor.

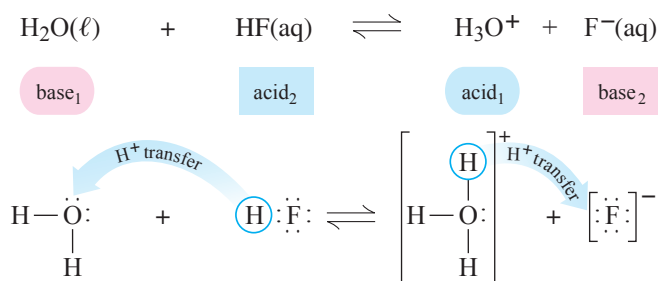


► Various measurements (electrical conductivity, freezing point depression, etc.) indicate that HF is only *slightly* ionized in water.

The positively charged proton is attracted to one of the two lone pairs on the oxygen atom. The ionization of hydrogen fluoride, a *weak* acid, is similar, but it occurs to only a slight extent, so we use a double arrow to indicate that it is reversible.



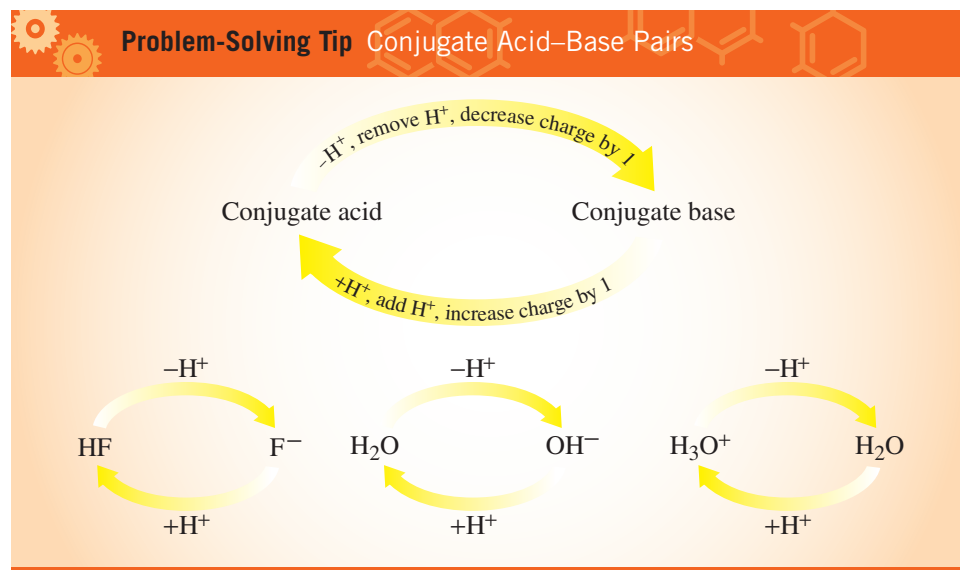
► Remember that in this text we use blue to indicate acids and red to indicate bases.



► The double arrow is used to indicate that the reaction occurs in both the forward and the reverse directions. It does not mean that there are equal amounts of reactants and products present. We use rectangles to indicate one conjugate acid–base pair and ovals to indicate the other pair.

We can describe Brønsted–Lowry acid–base reactions in terms of **conjugate acid–base pairs**. These are two species that differ by a proton. In the preceding equation, HF (acid₂) and F^- (base₂) are one conjugate acid–base pair, and H_2O (base₁) and H_3O^+ (acid₁) are the other pair. The members of each conjugate pair are designated by the same numerical subscript. In the forward reaction, HF and H_2O act as acid and base, respectively. In the reverse reaction, H_3O^+ acts as the acid, or proton donor, and F^- acts as the base, or proton acceptor.

► It makes no difference which conjugate acid–base pair, HF and F^- or H_3O^+ and H_2O , is assigned the subscripts 1 and 2.



A bottle of hydrochloric acid (HCl , left) releases gaseous hydrogen chloride that reacts with gas phase ammonia (NH_3 , right, from an aqueous ammonia solution) in an acid–base reaction. This produces the salt ammonium chloride (NH_4Cl) as very small solid particles (“smoke”).

Unless otherwise noted, all content on this page is © Cengage Learning.

► Base strength: $F^- > H_2O$ and $H_2O > Cl^-$; therefore $F^- > Cl^-$.

STOP & THINK

Be sure you fully understand this very important concept in acid–base chemistry.

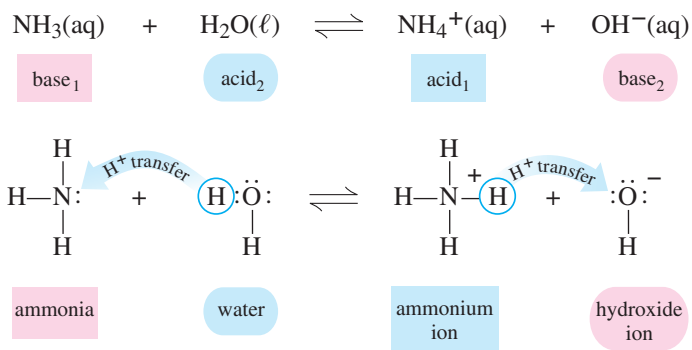
When the *weak* acid, HF, dissolves in water, the HF molecules give up some H^+ ions that can be accepted by either of two bases, F^- or H_2O . The fact that HF is only slightly ionized tells us that F^- is a *stronger* base than H_2O . When the *strong* acid, HCl, dissolves in water, the HCl molecules give up H^+ ions that can be accepted by either of two bases, Cl^- or H_2O . The fact that HCl is completely ionized in dilute aqueous solution tells us that Cl^- is a *weaker* base than H_2O . Thus, the weaker acid, HF, has the stronger conjugate base, F^- , while the stronger acid, HCl, has the weaker conjugate base, Cl^- . We can generalize:

The stronger the acid, the weaker is its conjugate base; the weaker the acid, the stronger is its conjugate base.

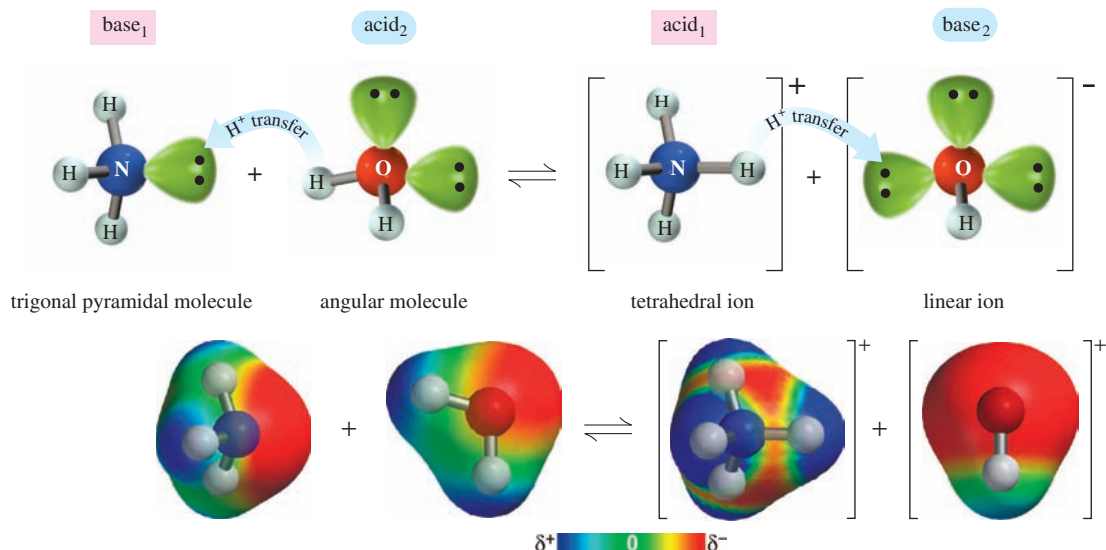
“Strong” and “weak,” like many other adjectives, are used here in a relative sense. When we say that the fluoride anion, F^- , is a stronger base than Cl^- ion we do *not* necessarily mean that it is a strong base in an absolute sense. For example, hydroxide ion, OH^- , is also a stronger base than Cl^- ion. That does not mean that hydroxide and fluoride ions have similar base strengths. In fact, the aqueous hydroxide ion is a far stronger base than the fluoride ion. “Stronger” and “weaker” are therefore just comparative terms that we use to compare the basicity (or acidity) of two ions or molecules. We often compare base strengths either to the hydroxide ion, which is a very strong base, or to the *anions of the strong acids*, which are very weak bases (e.g., Cl^- , Br^- , I^- , NO_3^-).

Ammonia acts as a weak Brønsted–Lowry base, and water acts as an acid in the ionization of aqueous ammonia.

► Be careful not to confuse *solubility in water* and *extent of ionization*. They are not necessarily related. Ammonia is very *soluble* in water (≈ 15 mol/L at $25^\circ C$). In a $0.10 M$ solution, NH_3 is only 1.3% ionized to form NH_4^+ and 98.7% nonionized.



As we see in the reverse reaction, ammonium ion, NH_4^+ , is the conjugate acid of NH_3 . The hydroxide ion, OH^- , is the conjugate base of water. The three-dimensional molecular structures are



Water acts as an acid (H^+ donor) in its reaction with NH_3 , whereas it acts as a base (H^+ acceptor) in its reactions with HCl and with HF .

Water can act either as an acid or as a base, depending on the other species present.

► The ability of a substance to react as either an acid or a base is known as amphotericism (see Section 10-6).

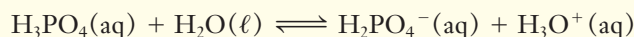
EXAMPLE 10-1 Identifying Conjugate Acid–Base Pairs

(a) Write the equation for the ionization of HNO_3 in water. (b) Identify the conjugate acid–base pairs in the equation for part (a). (c) What is the conjugate base of H_3PO_4 ? (d) What is the conjugate acid of SO_4^{2-} ?

Plan

When an acid ionizes (loses H^+) the deprotonated product (often anionic) is the conjugate base, while a base that reacts with H^+ forms a protonated product that is the conjugate acid.

- (a) HNO_3 is a strong acid and ionizes in water to produce NO_3^- (aq) and H_3O^+ (H^+).
- (b) HNO_3 is an acid, and its conjugate base is NO_3^- ; H_2O is a base, and H_3O^+ is the conjugate acid.
- (c) H_3PO_4 is an acid that reacts with water via the following equation:



In this reaction the H_2PO_4^- (aq) is the conjugate base to the H_3PO_4 (aq) acid.

- (d) SO_4^{2-} (aq) can react as a base with H^+ to form the conjugate acid HSO_4^- (aq).

Solution

- acid₁ base₂ base₁ acid₂
- (a) $\text{HNO}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \longrightarrow \text{NO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 - (b) Conjugate acid/base pairs for the preceding reaction:
 - HNO_3 (acid) and NO_3^- (conjugate base)
 - H_2O (base) and H_3O^+ (conjugate acid)
 - (c) Conjugate base of H_3PO_4 : H_2PO_4^-
 - (d) Conjugate acid of SO_4^{2-} : HSO_4^-

STOP & THINK

Study this example carefully. It is very important to be able to write balanced equations for reactions of acids and bases. You *must* be able to identify conjugate acids and conjugate bases.

$\text{B}-\text{H}$, $\text{C}-\text{H}$, and $\text{N}-\text{H}$ bonds in neutral molecules are usually too strong to ionize to produce H^+ . Most acids have H bonded to an electronegative atom such as O (especially when the O atom is bonded to an electronegative element in a high oxidation state) or to a halogen (F, Cl, Br, I). $\text{N}-\text{H}$ bonds to cationic nitrogen atoms are also weakly acidic (for example, NH_4^+).

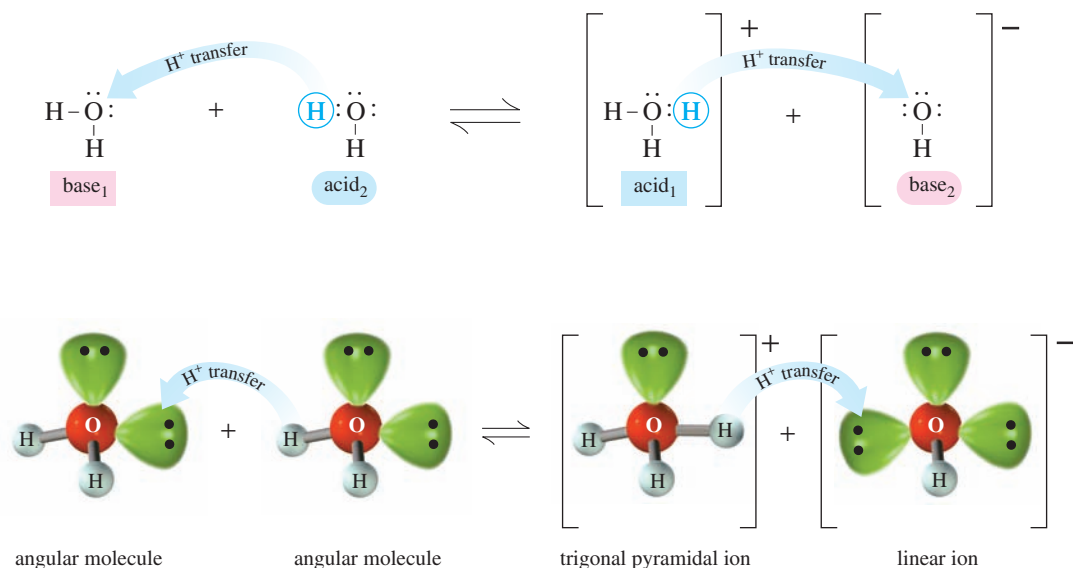
Bases must have at least one lone pair on an atom to be able to form a new bond to H^+ . Lone pairs on nitrogen and oxygen are the most common basic sites in molecules (e.g., NH_3 and H_2O). Anions, whether monatomic or polyatomic, typically have lone pairs that are basic; examples are F^- , OH^- , and PO_4^{3-} .

10-5 The Autoionization of Water

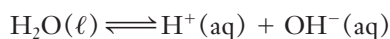
Careful measurements show that pure water ionizes ever so slightly to produce equal numbers of hydrated hydrogen ions and hydroxide ions.

Unless otherwise noted, all content on this page is © Cengage Learning.

► Because equal numbers of H^+ and OH^- ions are produced, the solution is neither acidic nor basic. This is referred to in acid–base terms as a *neutral* solution.



We have represented this reaction as $2\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$, but we will often show it in the simplified notation



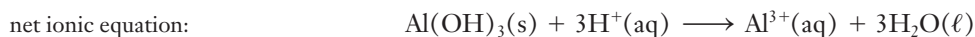
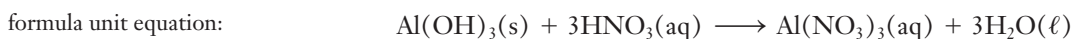
This **autoionization** (self-ionization) of water is an acid–base reaction according to the Brønsted–Lowry theory. One H_2O molecule (the acid) donates a proton to another H_2O molecule (the base). The H_2O molecule that donates a proton becomes an OH^- ion, the conjugate base of water. The H_2O molecule that accepts a proton becomes an H_3O^+ ion. Examination of the reverse reaction (right to left) shows that H_3O^+ (an acid) donates a proton to OH^- (a base) to form two H_2O molecules. One H_2O molecule behaves as an acid and the other acts as a base in the autoionization of water. Water is said to be **amphiprotic**; that is, H_2O molecules can both donate and accept protons.

As we saw in Section 6-9, Part 1, H^+ (or H_3O^+) ions and OH^- ions combine to form nonionized water molecules when strong acids and strong soluble bases react to form soluble salts and water. The reverse reaction, the autoionization of water, occurs only slightly, as expected.

10-6 Amphoterism

As we have seen, whether a particular substance behaves as an acid or as a base depends on its environment. Earlier we described the amphiprotic nature of water. **Amphoterism** is a more general term that describes the ability of a substance to react either as an acid or as a base. *Amphiprotic behavior* describes the cases in which substances exhibit amphoterism by accepting and by donating a proton, H^+ . Several *insoluble* metal hydroxides are amphoteric; that is, they react with acids to form salts and water, but they also dissolve in and react with excess strong bases.

Aluminum hydroxide is a typical amphoteric metal hydroxide. Its behavior as a *base* is illustrated by its reaction with nitric acid to form a *normal salt*. The balanced formula unit, total ionic, and net ionic equations for this reaction are, respectively:



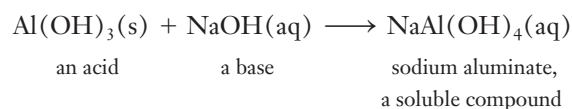
► A normal salt (see Section 10-9) contains no ionizable H atoms or OH groups.

Unless otherwise noted, all content on this page is © Cengage Learning.

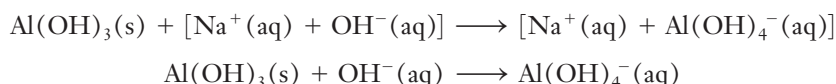
Table 10-1 Some Amphoteric Hydroxides

Metal or Metalloid Ions	Insoluble Amphoteric Hydroxide	Complex Ion Formed in an Excess of a Strong Base
Be ²⁺	Be(OH) ₂	[Be(OH) ₄] ²⁻
Al ³⁺	Al(OH) ₃	[Al(OH) ₄] ⁻
Cr ³⁺	Cr(OH) ₃	[Cr(OH) ₄] ⁻
Zn ²⁺	Zn(OH) ₂	[Zn(OH) ₄] ²⁻
Sn ²⁺	Sn(OH) ₂	[Sn(OH) ₃] ⁻
Sn ⁴⁺	Sn(OH) ₄	[Sn(OH) ₆] ²⁻
Pb ²⁺	Pb(OH) ₂	[Pb(OH) ₄] ²⁻
As ³⁺	As(OH) ₃	[As(OH) ₄] ⁻
Sb ³⁺	Sb(OH) ₃	[Sb(OH) ₄] ⁻
Si ⁴⁺	Si(OH) ₄	SiO ₄ ⁴⁻ and SiO ₃ ²⁻
Co ²⁺	Co(OH) ₂	[Co(OH) ₄] ²⁻
Cu ²⁺	Cu(OH) ₂	[Cu(OH) ₄] ²⁻

When an excess of a solution of any strong base, such as NaOH, is added to solid aluminum hydroxide, the Al(OH)₃ acts as an acid and dissolves. The equation for the reaction is usually written



The total ionic and net ionic equations are



Other amphoteric metal hydroxides undergo similar reactions.

Table 10-1 lists the common amphoteric hydroxides. Three are hydroxides of metalloids, As, Sb, and Si, which are located along the line that divides metals and nonmetals in the periodic table.

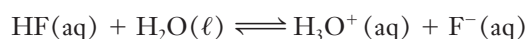
► All hydroxides containing small, highly charged metal ions are insoluble in water.

► Generally, elements of intermediate electronegativity form amphoteric hydroxides. Those of high and low electronegativity form acidic and basic “hydroxides,” respectively.

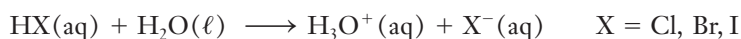
10-7 Strengths of Acids

Binary Acids

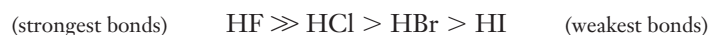
The ease of ionization of binary protic acids depends on both (1) the ease of breaking H—X bonds and (2) the stability of the resulting ions in solution. Let us consider the relative strengths of the Group 7A hydrohalic acids. Hydrogen fluoride ionizes only slightly in dilute aqueous solutions.



HCl, HBr, and HI, however, ionize completely or nearly completely in dilute aqueous solutions because the H—X bonds are much weaker.

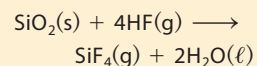


The order of *bond strengths* for the hydrogen halides is



STOP & THINK

A *weak* acid may be very reactive. For example, HF dissolves sand and glass. The equation for its reaction with sand is



The reaction with glass and other silicates is similar. These reactions are *not* related to acid strength; none of the three *strong* hydrohalic acids (HCl, HBr, or HI) undergoes such a reaction.

To understand why HF is a much weaker acid than the other hydrogen halides, let us consider the following factors.

1. *In HF the electronegativity difference is 1.9, compared with 0.9 in HCl, 0.7 in HBr, and 0.4 in HI (see Section 7-9). We might expect the very polar H—F bond in HF to ionize easily. The fact that HF is the *weakest* of these acids suggests that this effect must be of minor importance.*
2. *The bond strength is considerably greater in HF than in the other three molecules.* This tells us that the H—F bond is harder to break than the H—Cl, H—Br, and H—I bonds.
3. *The small, highly charged F[−] ion, formed when HF ionizes, causes increased ordering of the water molecules.* This increase is unfavorable to the process of ionization.

► Bond strength is shown by the bond energies introduced in Chapter 7 and discussed more fully in Section 15-9. The strength of the H—F bond is due largely to the very small size of the F atom and the strong ionic attraction between the F[−] and the H⁺ ions.

The net result of all factors is that HF is a much weaker acid than the other hydrohalic acids: HCl, HBr, and HI.

In dilute aqueous solutions, hydrochloric, hydrobromic, and hydroiodic acids are completely ionized, and all show the same apparent acid strength. Water is sufficiently basic that it does not distinguish among the acid strengths of HCl, HBr, and HI, and therefore it is referred to as a *leveling solvent* for these acids. It is not possible to determine the order of the strengths of these three acids in water because they are so nearly completely ionized.

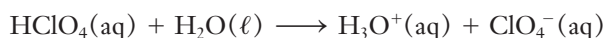
When these compounds dissolve in anhydrous acetic acid or other solvents less basic than water, however, they exhibit significant differences in their acid strengths. The observed order of acid strengths is



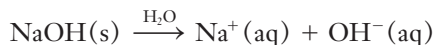
We observe that

the hydronium ion is the strongest acid that can exist in aqueous solution. All acids stronger than H₃O⁺(aq) react completely with water to produce H₃O⁺(aq) and their conjugate bases.

This is called the **leveling effect** of water. For example HClO₄ (Table 10-2) reacts completely with H₂O to form H⁺(aq) and ClO₄[−](aq).



Similar observations have been made for aqueous solutions of strong bases such as NaOH and KOH. Both are completely dissociated in dilute aqueous solutions.



► The amide ion, NH₂[−], is a stronger base than OH[−].

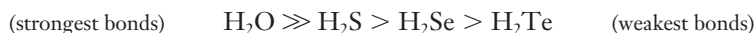
The hydroxide ion is the strongest base that can exist in aqueous solution. Bases stronger than OH[−] react completely with H₂O to produce OH[−] and their conjugate acids.

When metal amides such as sodium amide, NaNH₂, are placed in H₂O, the amide ion, NH₂[−], reacts with H₂O completely to produce NH₃ and OH[−].



Thus, we see that H₂O is a leveling solvent for all bases stronger than OH[−].

Acid strengths for binary acids of elements in other groups of the periodic table vary in the same way as those of the 7A elements. The order of bond strengths for the 6A hydrides is



H—O bonds are much stronger than the bonds in the other Group VI hydrides. As we might expect, the order of acid strengths for these hydrides is just the reverse of the order of bond strengths.



STOP & THINK

The trends in binary acid strengths *across* a period (e.g., CH₄ < NH₃ < H₂O < HF) are not those predicted from trends in bond energies and electronegativity differences. The correlations used for *vertical* trends cannot be used for *horizontal* trends. This is because a “horizontal” series of compounds have different stoichiometries and different numbers of unshared pairs of electrons on the central atoms.

Table 10-2 Relative Strengths of Conjugate Acid–Base Pairs

Acid		Base	
Acid strength increases	HClO₄ HI HBr HCl HNO₃	Negligible base strength in water.	ClO₄⁻ I⁻ Br⁻ Cl⁻ NO₃⁻
	acid loses H⁺ ↔ base gains H⁺		
	H₃O⁺ HF CH₃COOH HCN NH₄⁺ H₂O NH₃		H₂O F⁻ CH₃COO⁻ CN⁻ NH₃ OH⁻ NH₂⁻
	Equilibrium mixture of nonionized molecules of acid, conjugate base, and H ⁺ (aq).		
	NH ₂ ⁻ reacts completely with H ₂ O to form OH ⁻ ; it cannot exist in aqueous solution.		
	Base strength increases		

Table 10-2 displays relative acid and base strengths of a number of conjugate acid–base pairs.

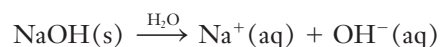
Ternary Acids

Most ternary acids (containing three different elements) are *hydroxyl compounds of non-metals* (oxoacids) that ionize to produce $\text{H}^+(\text{aq})$. The formula for nitric acid is commonly written HNO_3 to emphasize the presence of an acidic hydrogen atom. The hydrogen atom is bonded to one of the oxygen atoms so it could also be written as HONO_2 (see margin).

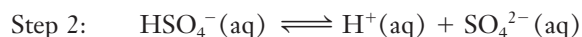
In most ternary acids the hydroxyl oxygen is bonded to a fairly electronegative non-metal. In nitric acid the nitrogen draws the electrons of the $\text{N}—\text{OH}$ bond closer to itself than would a less electronegative element such as sodium. The oxygen pulls the electrons of the $\text{O}—\text{H}$ bond close enough so that the hydrogen atom easily ionizes as H^+ , leaving NO_3^- . The regions of positive charge in HNO_3 are shown in blue in the electrostatic charge potential plot (margin).



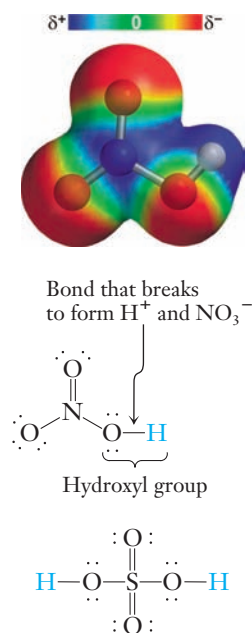
Let us consider the hydroxyl compounds of metals. We call these compounds *hydroxides* because they can produce hydroxide ions in water to give basic solutions. Oxygen is much more electronegative than most metals, such as sodium. It draws the electrons of the sodium–oxygen bond in NaOH (a strong base) so close to itself that the bonding is ionic. NaOH therefore exists as Na^+ and OH^- ions, even in the solid state, and dissociates into Na^+ and OH^- ions when it dissolves in H_2O .



Returning to our consideration of ternary acids, we usually write the formula for sulfuric acid as H_2SO_4 to emphasize that it is a polyprotic acid. The formula can also be written as $(\text{HO})_2\text{SO}_2$, however, because the structure of sulfuric acid (see margin) shows clearly that H_2SO_4 contains two $\text{O}—\text{H}$ groups bound to a sulfur atom. Because the $\text{O}—\text{H}$ bonds are easier to break than the $\text{S}—\text{O}$ bonds, sulfuric acid ionizes as an acid.



The first step in the ionization of H_2SO_4 is complete in aqueous solution. The second step is nearly complete in very dilute aqueous solutions. The first step in the ionization of



► Sulfuric acid is called a **polyprotic acid** because it has more than one ionizable hydrogen atom per molecule. It is the only *common* polyprotic acid that is also a strong acid.

Unless otherwise noted, all content on this page is © Cengage Learning.

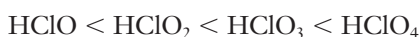
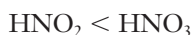
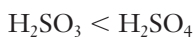
a polyprotic acid always occurs to a greater extent than the second step because it is easier to remove a proton from a neutral acid molecule than from a negatively charged anion.

Sulfurous acid, H_2SO_3 , is a polyprotic acid that contains the same elements as H_2SO_4 , but with one fewer electronegative, electron-withdrawing oxygen atom. This makes H_2SO_3 a weaker acid, which tells us that the $\text{H}-\text{O}$ bonds in H_2SO_3 are stronger than those in H_2SO_4 .

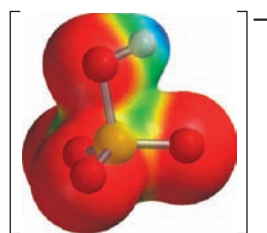
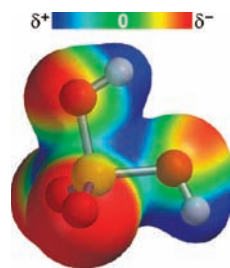
Similarly, comparison of the acid strengths of nitric acid, HNO_3 , and nitrous acid, HNO_2 , shows that HNO_3 is a much stronger acid than HNO_2 .

Acid strengths of most ternary acids containing the same central element increase with increasing oxidation state of the central element and with increasing numbers of oxygen atoms.

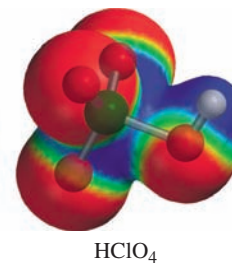
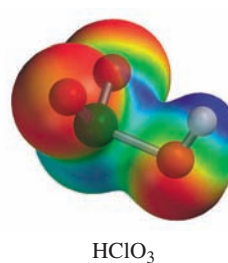
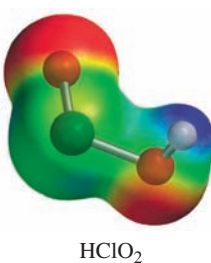
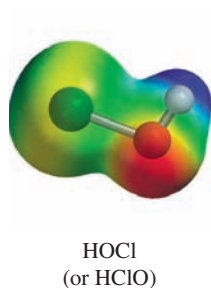
The following orders of increasing acid strength are typical.



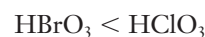
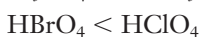
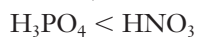
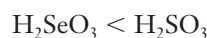
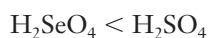
(strongest acids
are on the right side)



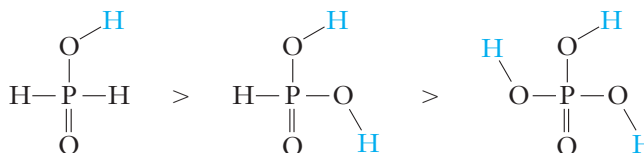
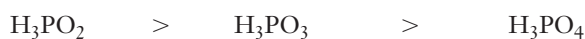
Electrostatic charge potential plots of H_2SO_4 (top) and HSO_4^- (bottom) showing the decrease in positive charge (blue) on the hydrogen atom in the anionic HSO_4^- . This explains the reduced acidity of HSO_4^- compared to H_2SO_4 .



For most ternary acids containing different elements from the same periodic table group, in the same oxidation state, acid strengths increase with increasing electronegativity of the central element.



Contrary to what we might expect, H_3PO_3 is a stronger acid than HNO_2 . Care must be exercised to compare acids that have *similar structures*. For example, H_3PO_2 , which has two H atoms bonded to the P atom, is a stronger acid than H_3PO_3 , which has one H atom bonded to the P atom. H_3PO_3 is a stronger acid than H_3PO_4 , which has no H atoms bonded to the P atom.



STOP & THINK

In most ternary inorganic acids, the H atoms are bonded to the O atoms. But it is very important to be sure of their structures before comparing them. The phosphorus-containing ternary acids are more complicated and can have both $\text{P}-\text{H}$ and $\text{O}-\text{H}$ bonding.

Strong Acids

Binary	Ternary
HCl	HClO_4
HBr	HClO_3
HI	HNO_3
	H_2SO_4

10-8 Acid–Base Reactions in Aqueous Solutions

In Section 6-9.1 we introduced classical acid–base reactions. We defined neutralization as the reaction of an acid with a base to form a salt and (in most cases) water. Most *salts* are ionic compounds that contain a cation other than H^+ and an anion other than OH^- or O^{2-} . The common *strong acids* and common *strong bases* are listed in the margin on pages 358–359. All other common acids may be assumed to be weak. The other common metal hydroxides (bases) are insoluble (or only slightly soluble) in water.

Arrhenius and Brønsted–Lowry acid–base neutralization reactions all have one thing in common.

Neutralization reactions involve the reaction of an acid with a base to form a salt that contains the cation characteristic of the base and the anion characteristic of the acid. Water is also usually formed.

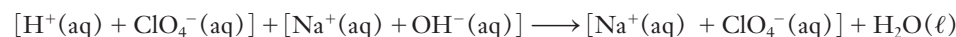
This is indicated in the formula unit equation. The general form of the net ionic equation, however, is different for different acid–base reactions. The net ionic equations depend on the solubility and extent of ionization or dissociation of each reactant and product.

In writing ionic equations, we always write the formulas of the predominant forms of the compounds in, or in contact with, aqueous solution. Writing ionic equations from formula unit equations requires a knowledge of the lists of strong acids and strong bases, as well as of the generalizations on solubilities of inorganic compounds. Please review carefully all of Sections 6-1 and 6-2. Study Tables 6-4 and 6-5 carefully because they summarize much information that you are about to use again.

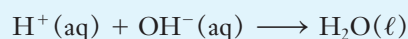
In Sections 6-1 and 6-9.1, we examined some reactions of strong acids with strong bases to form soluble salts. Let us illustrate one additional example. Perchloric acid, HClO_4 , reacts with sodium hydroxide to produce sodium perchlorate, NaClO_4 , a soluble salt.



The total ionic equation for this reaction is

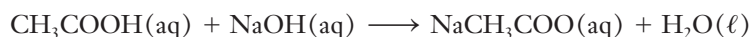


Eliminating the spectator ions, Na^+ and ClO_4^- , gives the net ionic equation



This is the net ionic equation for the reaction of all strong acids with strong bases to form soluble salts and water.

Many weak acids react with strong bases to form soluble salts and water. For example, acetic acid, CH_3COOH , reacts with sodium hydroxide, NaOH , to produce sodium acetate, NaCH_3COO .



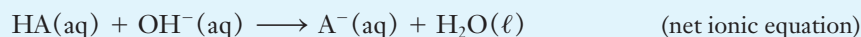
The total ionic equation for this reaction is



Elimination of Na^+ from both sides gives the net ionic equation



In general terms, the reaction of a *weak monoprotic acid* with a *strong base* to form a *soluble salt* may be represented as

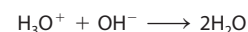


The reaction of a strong acid with a strong base to form a soluble salt and the reaction of a weak acid and a strong base to form a soluble salt were displayed earlier. Similar equations can be written for: (1) a strong acid reacting with a strong base to produce an insoluble salt and water, (2) a weak acid reacting with a strong base to produce an insoluble salt and water, (3) a strong acid reacting with a weak base to produce a soluble salt, and (4) a weak acid reacting with a weak base to produce a soluble salt. There are no common examples of a weak base reacting with either a weak or a strong Brønsted–Lowry acid to produce an insoluble salt. Each of the six types of reactions can be represented in general terms by its own unique net ionic equation.

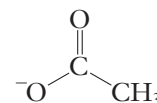
Strong Bases

LiOH	
NaOH	
KOH	$\text{Ca}(\text{OH})_2$
RbOH	$\text{Sr}(\text{OH})_2$
CsOH	$\text{Ba}(\text{OH})_2$

► This is considered to be the same as



► The acetate anion has the following structure:



► Monoprotic acids contain one, diprotic acids contain two, and triprotic acids contain three acidic (ionizable) hydrogen atoms per formula unit. Polyprotic acids (those that contain more than one ionizable hydrogen atom) are discussed in detail in Chapter 18.

CHEMISTRY IN USE

Everyday Salts of Ternary Acids

You may have encountered some salts of ternary acids without even being aware of them. For example, the iron in many of your breakfast cereals and breads may have been added in the form of iron(II) sulfate, FeSO_4 , or iron(II) phosphate, $\text{Fe}_3(\text{PO}_4)_2$; the calcium in these foods often comes from the addition of calcium carbonate, CaCO_3 . Fruits and vegetables keep fresh longer after an application of sodium sulfite, Na_2SO_3 , and sodium hydrogen sulfite, NaHSO_3 . Restaurants also use these two sulfites to keep their salad bars more appetizing. The red color of fresh meat is maintained for much longer by the additives sodium nitrate, NaNO_3 , and sodium nitrite, NaNO_2 . Sodium phosphate, Na_3PO_4 , is used to prevent metal ion flavors and to control acidity in some canned goods.

Many salts of ternary acids are used in medicine. Lithium carbonate, Li_2CO_3 , has been used successfully to combat severe jet lag. Lithium carbonate is also useful in the treatment of mania, depression, alcoholism, and schizophrenia. Magnesium sulfate, MgSO_4 , sometimes helps to prevent convulsions during pregnancy and to reduce the solubility of toxic barium sulfate in internally administered preparations consumed before gastrointestinal X-ray films are taken.

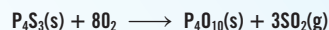
Other salts of ternary acids that you may find in your home include potassium chlorate, KClO_3 , in matches as an oxidizing agent and oxygen source; sodium hypochlorite, NaClO , in bleaches and mildew removers; and ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$, which is the primary ingredient in smelling salts.

► When all the H^+ from the acid and all the OH^- of the base have reacted, we say that there has been *complete neutralization*.



Charles Steele

The tips of “strike anywhere” matches contain tetraphosphorus trisulfide, red phosphorus, and potassium chlorate. Friction converts kinetic energy into heat, which initiates a spontaneous reaction.



The thermal decomposition of KClO_3 provides additional oxygen for this reaction.

Limestone and marble are calcium carbonate; gypsum and plaster of Paris are primarily calcium sulfate, CaSO_4 . Fireworks get their brilliant colors from salts such as barium nitrate, $\text{Ba}(\text{NO}_3)_2$, which imparts a green color; strontium carbonate, SrCO_3 , which gives a red color; and copper(II) sulfate, CuSO_4 , which produces a blue color. Should your fireworks get out of hand and accidentally start a fire, the ammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$, sodium hydrogen carbonate, NaHCO_3 , and potassium hydrogen carbonate, KHCO_3 , in your ABC dry fire extinguisher will come in handy.

RONALD DELORENZO

MIDDLE GEORGIA COLLEGE

EXAMPLE 10-2 Equations for Acid–Base Reactions

Write (a) formula unit, (b) total ionic, and (c) net ionic equations for the complete neutralization of phosphoric acid, H_3PO_4 , with potassium hydroxide, KOH .

Plan

- The salt produced in the reaction contains the cation of the base, K^+ , and the PO_4^{3-} anion of the acid. The salt is K_3PO_4 .
- H_3PO_4 is a weak acid—it is not written in ionic form. KOH is a strong base, and so it is written in ionic form. K_3PO_4 is a *soluble salt*, and so it is written in ionic form.
- The spectator ions are canceled to give the net ionic equation.

Solution

- $\text{H}_3\text{PO}_4(\text{aq}) + 3\text{KOH}(\text{aq}) \longrightarrow \text{K}_3\text{PO}_4(\text{aq}) + 3\text{H}_2\text{O}(\ell)$
- $\text{H}_3\text{PO}_4(\text{aq}) + 3[\text{K}^+(\text{aq}) + \text{OH}^-(\text{aq})] \longrightarrow [3\text{K}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})] + 3\text{H}_2\text{O}(\ell)$
- $\text{H}_3\text{PO}_4(\text{aq}) + 3\text{OH}^-(\text{aq}) \longrightarrow \text{PO}_4^{3-}(\text{aq}) + 3\text{H}_2\text{O}(\ell)$

You should now work Exercise 50.

EXAMPLE 10-3 Equations for Acid–Base Reactions

Write (a) formula unit, (b) total ionic, and (c) net ionic equations for the neutralization of aqueous ammonia with nitric acid.

Plan

- (a) The salt produced in the reaction contains the cation of the base, NH_4^+ , and the anion of the acid, NO_3^- . The salt is NH_4NO_3 .
- (b) HNO_3 is a strong acid—we write it in ionic form. Ammonia is a weak base. NH_4NO_3 is a soluble salt that is completely dissociated—we write it in ionic form.
- (c) We cancel the spectator ions, NO_3^- , and obtain the net ionic equation.

Solution

- (a) $\text{HNO}_3(\text{aq}) + \text{NH}_3(\text{aq}) \longrightarrow \text{NH}_4\text{NO}_3(\text{aq})$
- (b) $[\text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})] + \text{NH}_3(\text{aq}) \longrightarrow [\text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq})]$
- (c) $\text{H}^+(\text{aq}) + \text{NH}_3(\text{aq}) \longrightarrow \text{NH}_4^+(\text{aq})$

You should now work Exercise 52.

► Neutralization reactions of ammonia, NH_3 , form salts but do not form water.

EXAMPLE 10-4 Preparation of Salts

Write the formula unit equation for the reaction of an acid and a base that will produce each of the following salts: (a) Na_3PO_4 , (b) $\text{Ca}(\text{ClO}_3)_2$, (c) MgSO_4 .

Plan

- (a) The salt contains the ions, Na^+ and PO_4^{3-} . Na^+ is the cation in the strong base, NaOH . PO_4^{3-} is the anion in the weak acid, H_3PO_4 . The reaction of NaOH with H_3PO_4 should therefore produce the desired salt plus water.
- (b) The cation, Ca^{2+} , is from the strong base, $\text{Ca}(\text{OH})_2$. The anion, ClO_3^- , is from the strong acid, HClO_3 . The reaction of $\text{Ca}(\text{OH})_2$ with HClO_3 will produce water and the desired salt.
- (c) MgSO_4 is the salt produced in the reaction of $\text{Mg}(\text{OH})_2(\text{s})$ and $\text{H}_2\text{SO}_4(\text{aq})$.

Solution

- (a) $\text{H}_3\text{PO}_4(\text{aq}) + 3\text{NaOH}(\text{aq}) \longrightarrow \text{Na}_3\text{PO}_4(\text{aq}) + 3\text{H}_2\text{O}(\ell)$
- (b) $2\text{HClO}_3(\text{aq}) + \text{Ca}(\text{OH})_2(\text{aq}) \longrightarrow \text{Ca}(\text{ClO}_3)_2(\text{aq}) + 2\text{H}_2\text{O}(\ell)$
- (c) $\text{H}_2\text{SO}_4(\text{aq}) + \text{Mg}(\text{OH})_2(\text{s}) \longrightarrow \text{MgSO}_4(\text{aq}) + 2\text{H}_2\text{O}(\ell)$

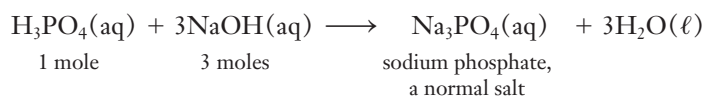
You should now work Exercise 54.



Ammonium chloride (NH_4Cl) is the white salt formed from the reaction of the base ammonia (NH_3) and hydrochloric acid (HCl). Heating NH_4Cl in a spoon produces some gaseous HCl and NH_3 that react again above the spoon to form white NH_4Cl “smoke.”

10-9 Acidic Salts and Basic Salts

To this point we have examined acid–base reactions in which stoichiometric amounts of Arrhenius acids and bases were mixed. Those reactions form *normal salts*. As the name implies, **normal salts** contain no ionizable H atoms or OH groups. The *complete* neutralization of phosphoric acid, H_3PO_4 , with sodium hydroxide, NaOH , produces the normal salt, Na_3PO_4 . The equation for this complete neutralization is



If less than a stoichiometric amount of a base reacts with a *polyprotic* acid, the resulting salt is classified as an **acidic salt**, because it can neutralize additional base.

Unless otherwise noted, all content on this page is © Cengage Learning.

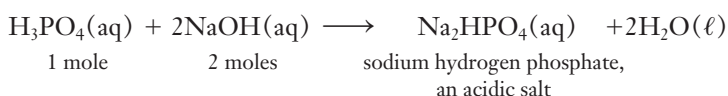
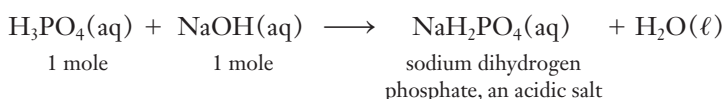


Charles D. Winters

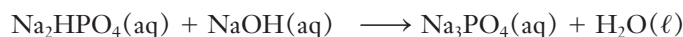
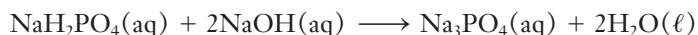
Sodium hydrogen carbonate, baking soda, is the most familiar example of an acidic salt. It can neutralize strong bases, but its aqueous solutions are slightly basic, as the blue color of the indicator bromthymol blue shows. NaHCO_3 (baking soda) is very handy for neutralizing chemical spills of acids or bases due to its ability to react with and neutralize both strong acids and strong bases. Containers of NaHCO_3 are kept in many chemistry labs for this purpose.

STOP & THINK

Remember that acidic and basic salts do not necessarily form solutions that are acidic or basic, respectively. The acidic and basic names refer to their ability to react with strong acids (basic salts) and bases (acidic salts). They can also often react with both acids and bases (e.g., NaHCO_3), but are usually named for their primary acid or base reaction chemistry.

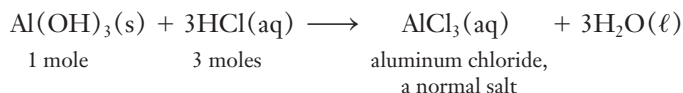


The reaction of phosphoric acid, H_3PO_4 , a weak acid, with strong bases can produce the three salts shown in the three preceding equations, depending on the relative amounts of acid and base used. The acidic salts, NaH_2PO_4 and Na_2HPO_4 , can react further with strong bases such as NaOH .

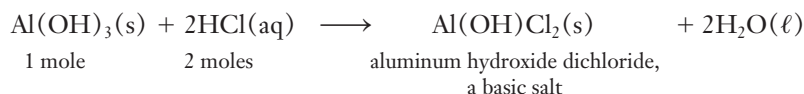
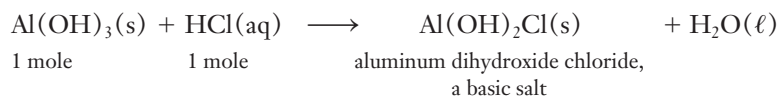


There are many additional examples of acidic salts. Sodium hydrogen carbonate, NaHCO_3 , commonly called sodium bicarbonate, is classified as an acidic salt. It is, however, the acidic salt of an extremely weak acid—carbonic acid, H_2CO_3 —and solutions of sodium bicarbonate are slightly basic, as are solutions of salts of other extremely weak acids.

Polyhydroxy bases (bases that contain more than one OH per formula unit) react with stoichiometric amounts of acids to form normal salts.



The reaction of a *polyhydroxy* base with less than a stoichiometric amount of an acid forms a **basic salt**, that is, a salt that contains unreacted OH groups. For example, the reaction of aluminum hydroxide with hydrochloric acid can produce two different basic salts:



Aqueous solutions of basic salts are not necessarily basic, but they can neutralize acids, for example,



Most basic salts are rather insoluble in water.



George Stanley

These basic aluminum salts are called “aluminum chlorohydrate.” They are components of some antiperspirants.

10-10 The Lewis Theory

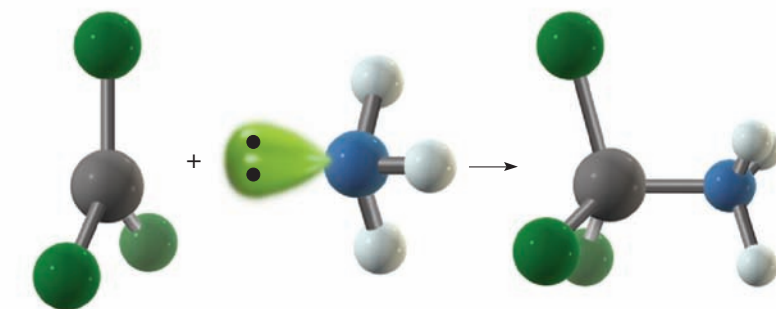
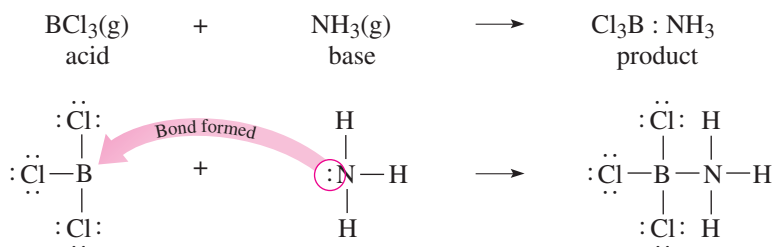
In 1923, Professor G. N. Lewis (1875–1946) presented the most comprehensive of the classic acid–base theories. The Lewis definitions follow.

► This is the same Lewis who made many contributions to our understanding of chemical bonding.

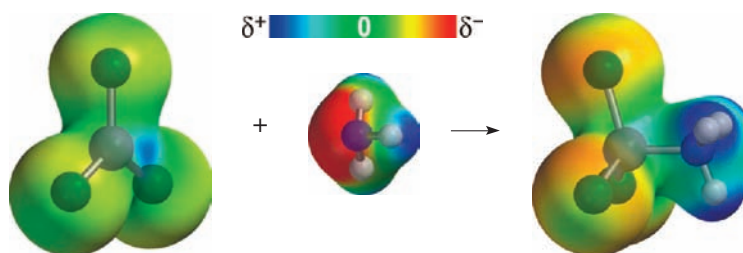
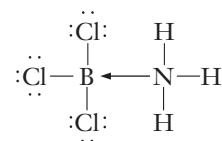
An **acid** is any species that can accept a share in an electron pair. A **base** is any species that can donate or share one or more lone pairs of electrons.

Lewis acids have low-lying empty valence orbitals that readily interact with lone pair(s) on other atoms (Lewis bases) to move towards a closed shell electronic configuration. These definitions do *not* specify that a lone pair of electrons must be transferred from one atom to another—only that an electron pair, residing originally on one atom (the Lewis base) must be shared with the Lewis acid. *Neutralization* is defined as **coordinate covalent** (or **dative**) **bond formation**. This results in a bond in which both electrons are furnished by one atom or ion (the Lewis base).

The reaction of boron trichloride with ammonia is a typical Lewis acid–base reaction. The Lewis theory is sufficiently general that it covers *all* acid–base reactions that the other theories include, plus many additional reactions such as metal complex formation (see Chapter 25).

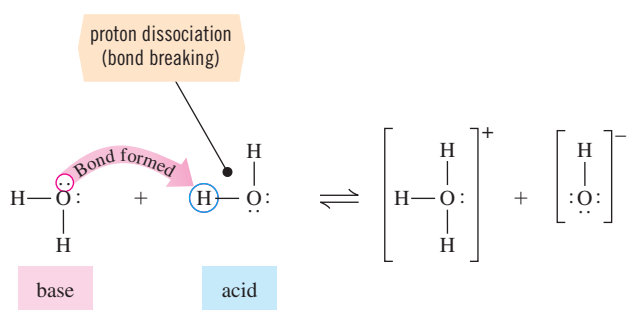


► In BCl_3 boron has an empty orbital and only 6 valence electrons. The sharing of the lone pair of electrons from the nitrogen with the boron brings the boron atom up to a filled octet of electrons. Chemists sometimes indicate a coordinate covalent or dative bond with an arrow to emphasize the donation of a lone pair of electrons from the Lewis base to Lewis acid.



Unless otherwise noted, all content on this page is © Cengage Learning.

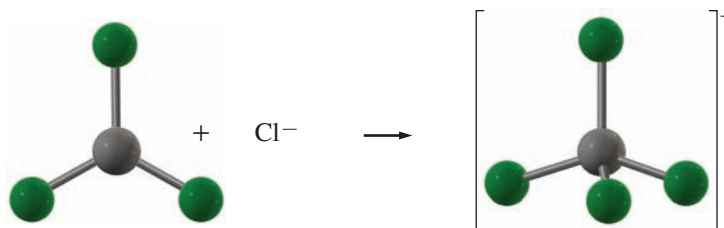
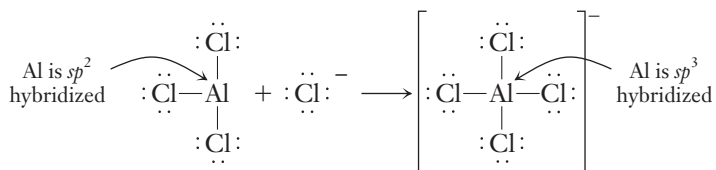
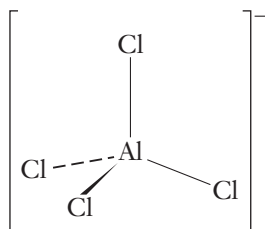
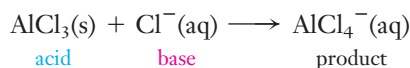
The autoionization of water (see Section 10-5) was described in terms of Brønsted–Lowry theory. In Lewis theory terminology, this is also an acid–base reaction. The acceptance of a proton, H^+ , by a base involves the formation of a coordinate covalent (dative) bond.



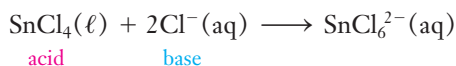
► Almost all transition metal complexes (see Chapter 25) form bonds by the donation of available electron pairs from surrounding atoms or molecules to vacant orbitals on the metal atom.

Theoretically, any species that contains a lone pair of electrons could act as a base. In fact, most ions and molecules that contain unshared electron pairs undergo some reactions by sharing their electron pairs with atoms or molecules that have low-energy vacant orbitals. Conversely, many Lewis acids contain only six electrons in the highest occupied energy level of the central element. They react by accepting a share in an additional pair of electrons from a Lewis base. Many compounds of the Group 3A elements are Lewis acids, as illustrated by the reaction of boron trichloride with ammonia, presented earlier.

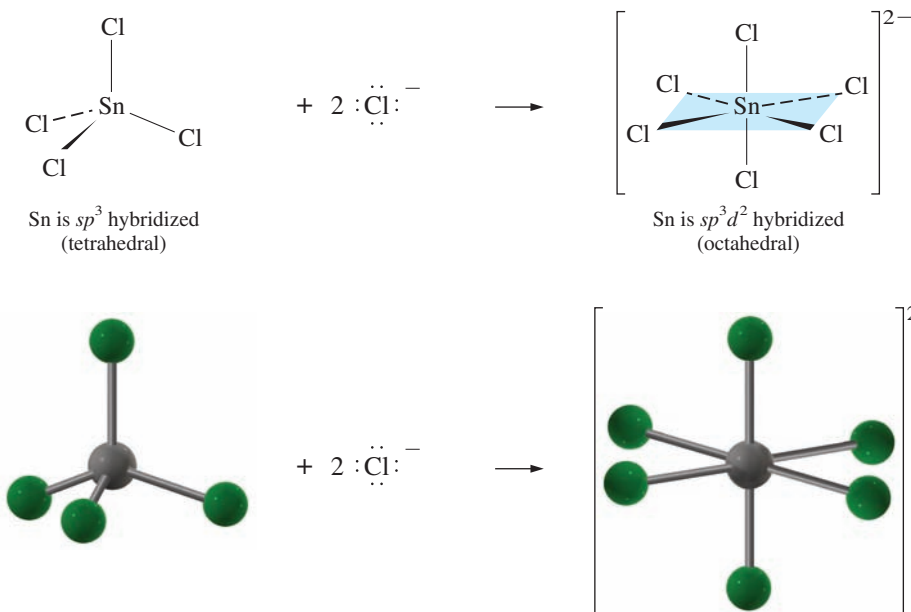
Anhydrous aluminum chloride, AlCl_3 , is a common Lewis acid that is used to catalyze many organic reactions. For instance, AlCl_3 acts as a Lewis acid when it dissolves in hydrochloric acid to give a solution that contains AlCl_4^- ions.



Other ions and molecules behave as Lewis acids by expansion of the valence shell of the central element, usually through the use of the next higher set of empty d orbitals. Anhydrous tin(IV) chloride is a colorless liquid that also is frequently used as a Lewis acid catalyst. It can accept shares in two additional electron pairs, as its reaction with hydrochloric acid illustrates.



Many organic and biological reactions are acid–base reactions that do not fit within the Arrhenius or Brønsted–Lowry theories. Experienced chemists find the Lewis theory to be very useful because so many other chemical reactions are covered by it.



► The term *volatile* describes a liquid or solution from which one of its components readily evaporates

Problem-Solving Tip Which Acid–Base Theory Should You Use?

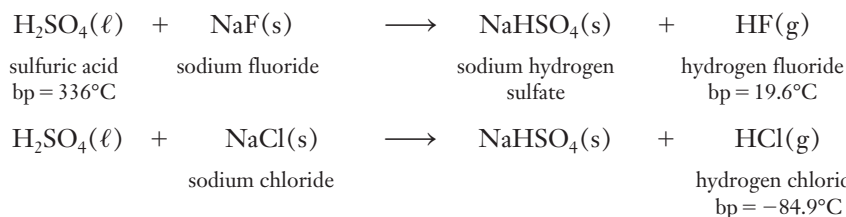
Remember the following:

1. Arrhenius acids and bases are also Brønsted–Lowry acids and bases; the reverse is not true.
2. Brønsted–Lowry acids and bases are also Lewis acids and bases; the reverse is not true.
3. We usually prefer the Arrhenius or the Brønsted–Lowry theory when water or another protic solvent is present.
4. Although the Lewis theory can be used to explain the acidic or basic property of some species in protic solvents, the most important use of the Lewis theory is for acid–base reactions in nonaqueous solvents and with transition metal complexes.

10-11 The Preparation of Acids

Some binary acids may be prepared by combination of the appropriate elements with hydrogen (see Section 5-8).

Small quantities of the hydrogen halides (their solutions are called hydrohalic acids) and other *volatile acids* are usually prepared by adding concentrated nonvolatile acids to the appropriate salts. (Sulfuric and phosphoric acids are classified as *nonvolatile acids* because they have much higher boiling points than other common acids.) The reactions of concentrated sulfuric acid with solid sodium fluoride and sodium chloride produce gaseous hydrogen fluoride and hydrogen chloride, respectively.

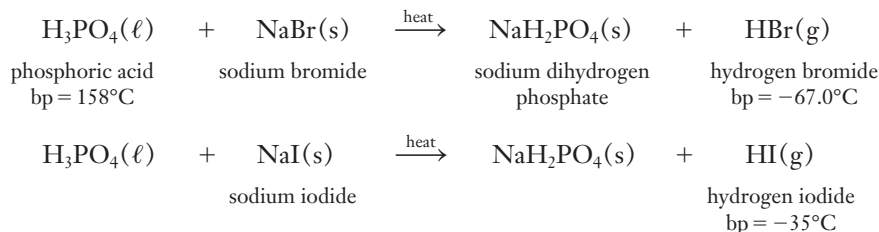


Charles D. Winters

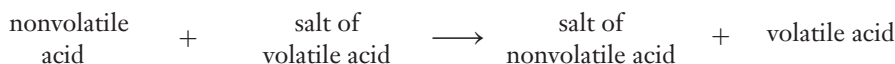
The volatile acid HCl can be made by dropping concentrated H_2SO_4 onto solid NaCl. Gaseous HCl is liberated. HCl(g) dissolves in the water on a piece of filter paper. The indicator methyl red on the paper turns red, its color in acidic solution.

Unless otherwise noted, all content on this page is © Cengage Learning.

Because concentrated sulfuric acid can act as an oxidizing agent, it cannot be used to prepare hydrogen bromide or hydrogen iodide; instead, the free halogens are produced. To produce hydrogen bromide or hydrogen iodide, phosphoric acid, a nonoxidizing acid, is dropped onto solid sodium bromide or sodium iodide, as the following equations show:

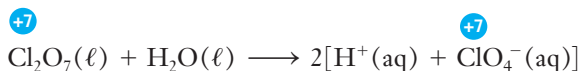


This kind of reaction may be generalized as

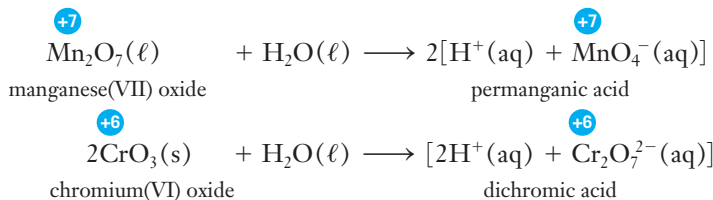


Dissolving each of the gaseous hydrogen halides in water gives the corresponding hydrohalic acid.

In Section 5-9, Part 2 we saw that many nonmetal oxides, called acid anhydrides, react with water to form *ternary acids* with no changes in oxidation numbers. For example, dichlorine heptoxide, Cl_2O_7 , forms perchloric acid when it dissolves in water.

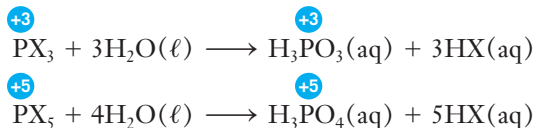


Some *high oxidation state transition metal oxides* are acidic oxides; that is, they dissolve in water to give solutions of ternary acids. Manganese(VII) oxide, Mn_2O_7 , and chromium(VI) oxide, CrO_3 , are the most common examples.

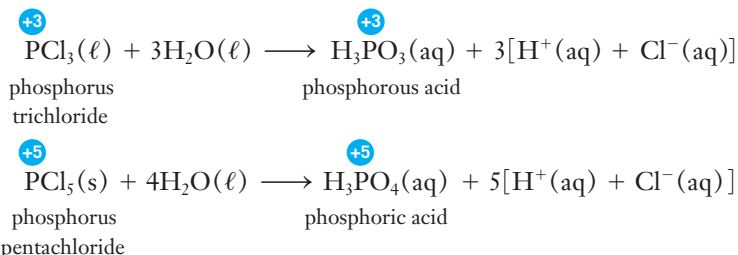


Neither permanganic acid nor dichromic acid has been isolated in pure form. Many stable salts of both are well known.

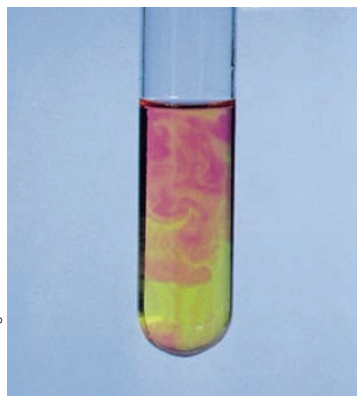
The halides and oxyhalides of some nonmetals hydrolyze (react with water) to produce two acids: a (binary) hydrohalic acid and a (ternary) oxyacid of the nonmetal. Phosphorus trihalides react with water to produce the corresponding hydrohalic acids and phosphorous acid, a weak diprotic acid, whereas phosphorus pentahalides give phosphoric acid and the corresponding hydrohalic acid. The phosphorus fluorides are an exception to this reactivity trend. The P — F bonds are generally too stable to react with water under mild to moderate conditions.



There are no changes in oxidation numbers in these reactions. Examples include the reactions of PCl_3 and PCl_5 with H_2O .



A solution of dichromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$ is deep red.



A drop of PCl_3 is added to water that contains the indicator methyl orange. As PCl_3 reacts with water to form HCl and H_3PO_3 , the indicator turns red, its color in acidic solution.

Unless otherwise noted, all content on this page is © Cengage Learning.

KEY TERMS

Acid (Arrhenius or Brønsted–Lowry) A substance that produces H^+ (aq) ions in aqueous solution. Strong acids ionize completely or almost completely in dilute aqueous solution; weak acids ionize only slightly.

Acid anhydride A nonmetal oxide that reacts with water to form an acid.

Acidic salt A salt that contains an ionizable hydrogen atom; does not necessarily produce acidic solutions.

Amphiprotism The ability of a substance to exhibit amphotericism by accepting or donating protons.

Amphoterism Ability of a substance to act as either an acid or a base.

Anhydrous Without water.

Autoionization An ionization reaction between identical molecules.

Base (Arrhenius) A substance that produces OH^- (aq) ions in aqueous solution. Strong bases are soluble in water and are completely *dissociated*. Weak bases ionize only slightly.

Basic anhydride A metal oxide that reacts with water to form a base.

Basic salt A salt containing a basic OH group.

Brønsted–Lowry acid A proton donor.

Brønsted–Lowry base A proton acceptor.

Brønsted–Lowry theory The description of an acid as a proton donor and a base as a proton acceptor; also known as the *Brønsted theory*.

Conjugate acid–base pair In Brønsted–Lowry terminology, a reactant and product that differ by a proton, H^+ .

Coordinate covalent bond A covalent bond in which both shared electrons are furnished by the same species; the bond between a Lewis acid and a Lewis base.

Dative bond See *Coordinate covalent bond*.

Dissociation In aqueous solution, the process in which a *solid ionic compound* separates into its ions.

Electrolyte A substance whose aqueous solutions conduct electricity.

Formula unit equation A chemical equation in which all compounds are represented by complete formulas.

Hydride A binary compound of hydrogen.

Hydronium ion H_3O^+ , the usual representation of the hydrated hydrogen ion.

Ionization In aqueous solution, the process in which a *molecular* compound reacts with water to form ions.

Leveling effect The effect by which all acids stronger than the acid that is characteristic of the solvent react with the solvent to produce that acid; a similar statement applies to bases. The strongest acid (base) that can exist in a given solvent is the acid (base) characteristic of that solvent.

Lewis acid Any species that can accept a share in an electron pair to form a coordinate covalent bond.

Lewis base Any species that can make available a share in an electron pair to form a coordinate covalent bond.

Net ionic equation The equation that results from canceling spectator ions and eliminating brackets from a total ionic equation.

Neutralization The reaction of an acid with a base to form a salt and (usually) water; usually, the reaction of hydrogen ions with hydroxide ions to form water molecules.

Nonelectrolyte A substance whose aqueous solutions do not conduct electricity.

Normal salt A salt that contains no ionizable H atoms or OH groups.

Polyprotic acid An acid that contains more than one ionizable hydrogen atom per formula unit.

Protic acid An Arrhenius acid, or a Brønsted–Lowry acid.

Salt A compound that contains a cation other than H^+ and an anion other than OH^- or O^{2-} .

Spectator ions Ions in solution that do not participate in a chemical reaction.

Strong electrolyte A substance that conducts electricity well in dilute aqueous solution.

Ternary acid An acid that contains three elements—usually H, O, and another nonmetal.

Ternary compound A compound that contains three different elements.

Total ionic equation The equation for a chemical reaction written to show the predominant form of all species in aqueous solution or in contact with water.

Weak electrolyte A substance that conducts electricity poorly in dilute aqueous solution.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

The Arrhenius Theory

1. ● Define and illustrate the following terms clearly and concisely. Give an example of each. (a) Strong electrolyte; (b) weak electrolyte; (c) nonelectrolyte; (d) strong acid; (e) strong base; (f) weak acid; (g) weak base; (h) insoluble base. (See Section 6-1.)

2. Outline Arrhenius' ideas about acids and bases. (a) How did he define the following terms: acid, base, neutralization? (b) Give an example that illustrates each term.
3. Classify each of these as an acid or a base. Which are strong and which are weak? What ions are produced when each is dissolved in water? (a) KOH ; (b) $\text{Mg}(\text{OH})_2$; (c) HClO ; (d) HBr ; (e) LiOH ; (f) H_2SO_3 .

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

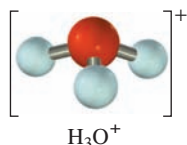
Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

- Describe an experiment for classifying compounds as strong electrolytes, weak electrolytes, or nonelectrolytes. Tell what would be observed for each of the following compounds and classify each: Na_2SO_4 ; HCN ; CH_3COOH ; CH_3OH ; HF ; HClO_4 ; HCOOH ; NH_3 . Compare your answer to the experiment described in Figure 6-1.
- Write formulas and names for (a) the common strong acids; (b) three weak acids; (c) the common strong bases; (d) the most common weak base; (e) four soluble salts; (f) four insoluble salts. (See Section 6-1.)
- Give the conjugate acids of each of the following: H_2O , OH^- , I^- , AsO_4^{3-} , NH_2^- , HPO_4^{2-} , and ClO_2^- .
- Give the conjugate bases of each of the following: H_2O , HS^- , HBr , PH_4^+ , and HOCH_3 .
- Identify the Brønsted–Lowry acids and bases in these reactions and group them into conjugate acid–base pairs.
 - $\text{NH}_3 + \text{HBr} \rightleftharpoons \text{NH}_4^+ + \text{Br}^-$
 - $\text{NH}_4^+ + \text{HS}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{S}$
 - $\text{H}_3\text{O}^+ + \text{PO}_4^{3-} \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_2\text{O}$
 - $\text{HSO}_3^- + \text{CN}^- \rightleftharpoons \text{HCN} + \text{SO}_3^{2-}$
 - $\text{O}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{OH}^-$

The Hydrated Hydrogen Ion

- Write the formula of a hydrated hydrogen ion that contains only one water of hydration. Give another name for the hydrated hydrogen ion.
- Why is the hydrated hydrogen ion important?
- Criticize the following statement: “The hydrated hydrogen ion should always be represented as H_3O^+ .”



Brønsted–Lowry Theory

- State the basic ideas of the Brønsted–Lowry theory.
- Use Brønsted–Lowry terminology to define the following terms. Illustrate each with a specific example. (a) acid; (b) conjugate base; (c) base; (d) conjugate acid; (e) conjugate acid–base pair.
- Write balanced equations that describe the ionization of the following acids in dilute aqueous solution. Use a single arrow ($\longrightarrow$) to represent complete, or nearly complete, ionization and a double arrow ($\rightleftharpoons$) to represent a small extent of ionization. (a) HBr ; (b) $\text{C}_2\text{H}_5\text{COOH}$; (c) H_2S ; (d) HCN ; (e) HF ; (f) HClO_4 .
- Use words and equations to describe how ammonia can act as a base in (a) aqueous solution and (b) the pure state, that is, as gaseous ammonia molecules, when it reacts with gaseous hydrogen chloride or a similar anhydrous acid.
- What does autoionization mean? How can the autoionization of water be described as an acid–base reaction? What structural features must a compound have to be able to undergo autoionization?
- Use equations to illustrate the fact that these species are bases in water: NH_3 ; HS^- ; CH_3COO^- ; O^{2-} .
- In terms of Brønsted–Lowry theory, state the differences between (a) a strong base and a weak base and (b) a strong acid and a weak acid. Write a net ionic equation of an example of each of these two types of reactions.
- Give the products in the following acid–base reactions. Identify the conjugate acid–base pairs.
 - $\text{NH}_4^+ + \text{CH}_3\text{COO}^-$; (b) $\text{S}^{2-} + \text{H}_2\text{SO}_4$;
 - $\text{HClO}_4 + [\text{H}_2\text{NNH}_3]^+$; (d) $\text{NH}_2^- + \text{H}_2\text{O}$
- Give the conjugate acids of each of the following: H_2O , OH^- , I^- , AsO_4^{3-} , NH_2^- , HPO_4^{2-} , and ClO_2^- .
- Give the conjugate bases of each of the following: H_2O , HS^- , HBr , PH_4^+ , and HOCH_3 .
- Identify the Brønsted–Lowry acids and bases in these reactions and group them into conjugate acid–base pairs.
 - $\text{NH}_3 + \text{HBr} \rightleftharpoons \text{NH}_4^+ + \text{Br}^-$
 - $\text{NH}_4^+ + \text{HS}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{S}$
 - $\text{H}_3\text{O}^+ + \text{PO}_4^{3-} \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_2\text{O}$
 - $\text{HSO}_3^- + \text{CN}^- \rightleftharpoons \text{HCN} + \text{SO}_3^{2-}$
 - $\text{O}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{OH}^-$
- Identify each species in the following reactions as either an acid or a base, in the Brønsted–Lowry sense.
 - $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$
 - $\text{HCO}_3^- + \text{H}_2\text{SO}_4 \rightleftharpoons \text{HSO}_4^- + \text{H}_2\text{CO}_3$
 - $\text{CH}_3\text{COOH} + \text{NO}_2^- \rightleftharpoons \text{HNO}_2 + \text{CH}_3\text{COO}^-$
 - $\text{NH}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{OH}^-$
- Identify each reactant and product in the following chemical reactions as a Brønsted–Lowry acid, a Brønsted–Lowry base, or neither. Arrange the species in each reaction as conjugate acid–base pairs.
 - $\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$
 - $\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{PO}_4^{3-}$
 - $\text{NH}_3 + \text{H}^- \rightleftharpoons \text{H}_2 + \text{NH}_2^-$
 - $\text{HCl} + \text{NH}_3 \rightleftharpoons \text{NH}_4\text{Cl}$
 - $\text{NH}_4^+ + \text{HSO}_3^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{SO}_3$
- In each of the following acid–base reactions, identify the Brønsted acid and base on the left and their conjugate partners on the right.
 - $\text{C}_5\text{H}_5\text{N}(\text{aq}) + \text{CH}_3\text{CO}_2\text{H}(\text{aq}) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(\text{aq}) + \text{CH}_3\text{CO}_2^-(\text{aq})$
 - $\text{N}_2\text{H}_4(\text{aq}) + \text{HSO}_4^-(\text{aq}) \rightleftharpoons \text{N}_2\text{H}_5^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
 - $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}(\text{aq}) + \text{H}_2\text{O}(\ell)$
- Arrange the species in the reactions of Exercise 20 as Brønsted–Lowry conjugate pairs.

Properties of Aqueous Solutions of Acids and Bases

- Write equations and designate conjugate pairs for the stepwise reactions in water of (a) H_2SO_4 and (b) H_2SO_3 .
- We say that strong acids, weak acids, and weak bases *ionize* in water, but strong bases *dissociate* in water. What is the difference between ionization and dissociation?
- List five properties of bases in aqueous solution. Does aqueous ammonia exhibit these properties? Why?
- List six properties of aqueous solutions of protic acids.

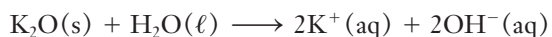
Amphoterism

- Use chemical equations to illustrate the hydroxides of beryllium, zinc, arsenic, and antimony reacting (a) as acids and (b) as bases.

29. Draw the Lewis formula of aluminum hydroxide, and explain the features that enable it to possess amphoteric properties.

Strengths of Acids

30. Briefly explain how the following reaction illustrates the leveling effect of water.



31. What property is characteristic of all strong acids and strong bases but not weak acids and weak bases?
32. What does base strength mean? What does acid strength mean?
33. Classify each of the following substances as (a) a strong soluble base, (b) an insoluble base, (c) a strong acid, or (d) a weak acid: KOH; HCl; Ba(OH)₂; Cu(OH)₂; H₂S; H₂CO₃; H₂SO₄; Zn(OH)₂.
34. (a) What are binary protic acids? (b) Write names and formulas for four binary protic acids.
35. (a) How can the order of increasing acid strength in a series of similar binary monoprotic acids be explained? (b) Illustrate your answer for the series HF, HCl, HBr, and HI. (c) What is the order of increasing base strength of the conjugate bases of the acids in (b)? Why? (d) Is your explanation applicable to the series H₂O, H₂S, H₂Se, and H₂Te? Why?
36. Arrange the members of each group in order of decreasing acidity: (a) H₂O, H₂Se, H₂S; (b) HI, HCl, HF, HBr; (c) H₂S, S²⁻, HS⁻.
37. (a) Which is the stronger acid of each pair? (1) NH₄⁺, NH₃; (2) H₂O, H₃O⁺; (3) HS⁻, H₂S; (4) HSO₃⁻, H₂SO₃. (b) How are acidity and charge related for each of these pairs?
38. Classify each of the compounds NaH, BeH₂, BH₃, CH₄, NH₃, H₂O, and HF as a Brønsted–Lowry base, a Brønsted–Lowry acid, or neither.
39. Illustrate the leveling effect of water by writing equations for the reactions of HCl and HNO₃ with water.

Ternary Acids

40. In what sense can we describe nitric and perchloric acids as hydroxyl compounds of nonmetals?
41. What are ternary acids? Write names and formulas for four monoprotic ternary acids.
42. Among the compounds formed by phosphorus are phosphoric acid (H₃PO₄) and phosphorous acid (H₃PO₃). H₃PO₄ is a triprotic acid, while H₃PO₃ is only diprotic. Draw Lewis formulas of these two compounds that would account for the triprotic nature of H₃PO₄ and the diprotic nature of H₃PO₃, and explain how your structures show this behavior. Suggest an alternative means of writing the formula of phosphorous acid that would better represent its acid–base behavior.
43. Explain the order of increasing acid strength for the following groups of acids and the order of increasing base

strength for their conjugate bases. (a) H₂SO₃, H₂SO₄; (b) HNO₂, HNO₃; (c) H₃PO₃, H₃PO₄; (d) HClO, HClO₂, HClO₃, HClO₄.

44. (a) Write a generalization that describes the order of acid strengths for a series of ternary acids that contain different elements in the same oxidation state from the same group in the periodic table. (b) Indicate the order of acid strengths for the following: (1) HNO₃, H₃PO₄; (2) H₃PO₄, H₃AsO₄; (3) H₂TeO₆, H₂SeO₄; (4) HClO₃, HBrO₃, HIO₃.
45. List the following acids in order of increasing strength: (a) sulfuric, phosphoric, and perchloric; (b) HIO₃, HIO₂, HIO, and HIO₄; (c) selenous, sulfurous, and tellurous acids; (d) hydrosulfuric, hydroselenic, and hydrotelluric acids; (e) H₂CrO₄, H₂CrO₂, HCrO₃, and H₃CrO₃.

Reactions of Acids and Bases

46. Why are acid–base reactions described as neutralization reactions?
47. Distinguish among (a) formula unit equations, (b) total ionic equations, and (c) net ionic equations. What are the advantages and limitations of each?
48. Classify each substance as either an electrolyte or a nonelectrolyte: NH₄Cl; HI; C₆H₆; RaF₂; Zn(CH₃COO)₂; Cu(NO₃)₂; CH₃COOH; C₁₂H₂₂O₁₁ (table sugar); KOH; KHCO₃; NaClO₄; La₂(SO₄)₃; I₂.
49. Classify each substance as either a strong or a weak electrolyte, and then list (a) the strong acids, (b) the strong bases, (c) the weak acids, and (d) the weak bases. NaCl; MgSO₄; HCl; CH₃COOH; Ba(NO₃)₂; H₃PO₄; Sr(OH)₂; HNO₃; HI; Ba(OH)₂; LiOH; C₃H₅COOH; NH₃; CH₃NH₂; KOH; HCN; HClO₄.

For Exercises 50–52, write balanced (1) formula unit, (2) total ionic, and (3) net ionic equations for reactions between the acid–base pairs. Name all compounds except water. Assume complete neutralization.

50. (a) HNO₂ + LiOH →
(b) H₂SO₄ + KOH →
(c) HCl + NH₃ →
(d) CH₃COOH + NaOH →
(e) HI + NaOH →
51. (a) H₂CO₃ + Ba(OH)₂ →
(b) H₂SO₄ + Ba(OH)₂ →
(c) H₃PO₄ + Ca(OH)₂ →
(d) HBr + NaOH →
(e) H₃AsO₄ + NaOH →
52. (a) HClO₄ + Ba(OH)₂ →
(b) HI + Ca(OH)₂ →
(c) H₂SO₄ + NH₃ →
(d) H₂SO₄ + Fe(OH)₃ →
(e) H₂SO₄ + Ba(OH)₂ →

53. Complete these equations by writing the formulas of the omitted compounds.
- $\text{Ba}(\text{OH})_2 + ? \longrightarrow \text{Ba}(\text{NO}_3)_2(\text{aq}) + 2\text{H}_2\text{O}$
 - $\text{FeO}(\text{s}) + ? \longrightarrow \text{FeCl}_2(\text{aq}) + \text{H}_2\text{O}$
 - $\text{HCl}(\text{aq}) + ? \longrightarrow \text{AgCl}(\text{s}) + ?$
 - $\text{Na}_2\text{O} + ? \longrightarrow 2\text{NaOH}(\text{aq})$
 - $\text{NaOH} + ? \longrightarrow \text{Na}_2\text{HPO}_4(\text{aq}) + ?$
(two possible answers)
54. Although many salts may be formed by a variety of reactions, salts are usually thought of as being derived from the reaction of an acid with a base. For each of the salts listed here, choose the acid and base that would react with each other to form the salt. Write the (i) formula unit, (ii) total ionic, and (iii) net ionic equations for the formation of each salt. (a) $\text{Pb}(\text{NO}_3)_2$; (b) SrCl_2 ; (c) $(\text{NH}_4)_2\text{SO}_4$; (d) $\text{Ca}(\text{ClO}_4)_2$; (e) $\text{Al}_2(\text{SO}_4)_3$.
55. (a) Which of the following compounds are salts? CaCO_3 ; Li_2O ; $\text{U}(\text{NO}_3)_5$; AgNO_3 ; $\text{Ca}(\text{CH}_3\text{COO})_2$. (b) Write an acid–base equation that accounts for the formation of those identified as being salts.
56. Repeat Exercise 55 for KMnO_4 , CaSO_4 , P_4O_{10} , SnF_2 , and K_3PO_4 .

Acidic and Basic Salts

57. What are polyprotic acids? Write names and formulas for five polyprotic acids.
58. What are acidic salts? Write balanced equations to show how the following acidic salts can be prepared from the appropriate acid and base: NaHSO_3 ; NaHCO_3 ; KH_2PO_4 ; Na_2HPO_4 ; NaHS .
59. Indicate the mole ratio of acid and base required in each case in Exercise 58.
60. The following salts are components of fertilizers. They are made by reacting gaseous NH_3 with concentrated solutions of acids. The heat produced by the reactions evaporates most of the water. Write balanced formula unit equations that show the formation of each. (a) NH_4NO_3 ; (b) $\text{NH}_4\text{H}_2\text{PO}_4$; (c) $(\text{NH}_4)_2\text{HPO}_4$; (d) $(\text{NH}_4)_3\text{PO}_4$; (e) $(\text{NH}_4)_2\text{SO}_4$.



Common lawn fertilizer

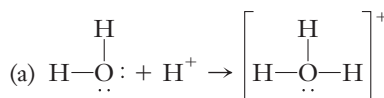
61. What are polyhydroxy bases? Write names and formulas for five polyhydroxy bases.

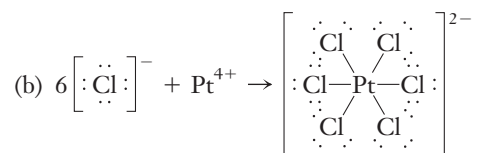
62. What are basic salts? (a) Write balanced equations to show how each of the following basic salts can be prepared from the appropriate acid and base: $\text{Ca}(\text{OH})\text{Cl}$; $\text{Al}(\text{OH})_2\text{Cl}$; $\text{Al}(\text{OH})\text{Cl}_2$. (b) Indicate the mole ratio of acid and base required in each case.
63. What are amphoteric metal hydroxides? (a) Are they bases? (b) Write the names and formulas for four amphoteric metal hydroxides.
64. Write stepwise equations for protonation or deprotonation of each of these polyprotic acids and bases in water. (a) CO_3^{2-} ; (b) H_3AsO_4 ; (c) $\text{NH}_2\text{CH}_2\text{COO}^-$ (glycinate ion, a diprotic base).
65. Write the chemical equations for the stepwise ionization of oxalic acid, $(\text{COOH})_2$, a diprotic acid.
66. Write the chemical equations for the stepwise ionization of citric acid, $\text{C}_3\text{H}_5\text{O}(\text{COOH})_3$, a triprotic acid.

The Lewis Theory

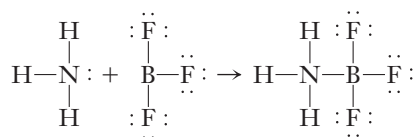
67. Define and illustrate the following terms clearly and concisely. Write an equation to illustrate the meaning of each term. (a) Lewis acid; (b) Lewis base; (c) neutralization according to Lewis theory.
68. Write a Lewis formula for each species in the following equations. Label the acids and bases using Lewis theory terminology.
- $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$
 - $\text{HCl}(\text{g}) + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$
 - $\text{NH}_3(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
 - $\text{NH}_3(\text{g}) + \text{HBr}(\text{g}) \longrightarrow \text{NH}_4\text{Br}(\text{s})$
69. Explain the differences between the Brønsted–Lowry and the Lewis acid–base theories, using the formation of the ammonium ion from ammonia and water to illustrate your points.
70. Identify the Lewis acid and the Lewis base in each reaction.
- $\text{I}_2(\text{s}) + \text{I}^-(\text{aq}) \longrightarrow \text{I}_3^-(\text{aq})$
 - $\text{SO}_2(\text{g}) + \text{BF}_3(\text{g}) \longrightarrow \text{O}_2\text{S}(\text{BF}_3)(\text{s})$
 - $\text{Au}^+(\text{aq}) + 2\text{CN}^-(\text{aq}) \longrightarrow [\text{Au}(\text{CN})_2]^-(\text{aq})$
 - $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell) \longrightarrow \text{H}_2\text{CO}_3(\text{aq})$
71. Decide whether each of the following substances should be classified as a Lewis acid or a Lewis base.
- BCl_3 (Hint: Draw the Lewis dot structure.)
 - H_2NNH_2 , hydrazine (Hint: Draw the Lewis dot structure.)
 - the reactants in the reaction

$$\text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$$
72. Identify the Lewis acid and base and the donor and acceptor atoms in each of the following reactions.

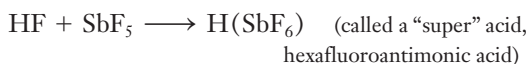




73. What is the term for a single covalent bond in which both electrons in the shared pair come from the same atom? Identify the Lewis acid and base and the donor and acceptor atoms in the following reaction.



74. A group of very strong acids are the fluoroacids, H_mXF_n . Two such acids are formed by Lewis acid–base reactions.
(a) Identify the Lewis acid and the Lewis base.



- (b) To which atom is the H of the product bonded? How is the H bonded?

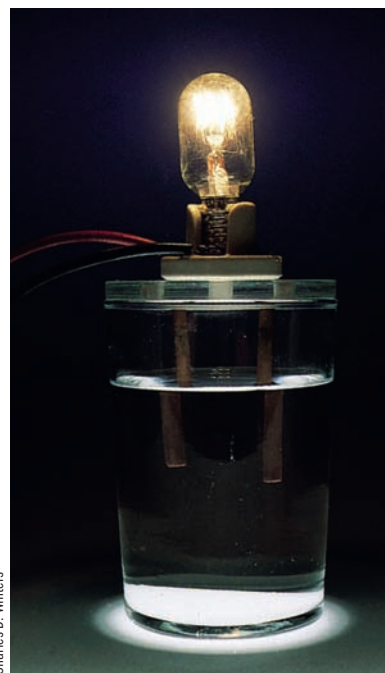
Preparation of Acids

75. A volatile acid such as nitric acid, HNO_3 , can be prepared by adding concentrated H_2SO_4 to a salt of the acid. (a) Write the chemical equation for the reaction of H_2SO_4 with sodium nitrate (called Chile salt peter). (b) A dilute aqueous solution of H_2SO_4 cannot be used. Why?
76. Outline a method of preparing each of the following acids, and write appropriate balanced equations for each preparation: (a) H_2S ; (b) HCl ; (c) CH_3COOH .
77. Repeat Exercise 76 for (a) carbonic acid, (b) chloric acid, (c) permanganic acid, and (d) phosphoric acid (two methods).

Mixed Exercises

78. Give the formula for an example chosen from the representative elements for (a) an acidic oxide, (b) an amphoteric oxide, and (c) a basic oxide.
79. Identify each of the following as (i) acidic, (ii) basic, or (iii) amphoteric. Assume all oxides are dissolved in or are in contact with water. Do not be intimidated by the way in which the formula of the compound is written. (a) ORb_2 ; (b) Cl_2O_5 ; (c) HCl ; (d) $\text{SO}_2(\text{OH})_2$; (e) HONO ; (f) Al_2O_3 ; (g) CaO ; (h) H_2O ; (i) CO_2 ; (j) OSO .
80. Indicate which of the following substances—(a) H_2S ; (b) $\text{PO}(\text{OH})_3$; (c) H_2CaO_2 ; (d) $\text{ClO}_3(\text{OH})$; (e) $\text{Sb}(\text{OH})_3$ —can act as (i) an acid, (ii) a base, or (iii) both according to the Arrhenius (classical) theory or the Brønsted–Lowry theory. Do not be confused by the way in which the formulas are written.

81. (a) Write equations for the reactions of HCO_3^- with H_3O^+ and HCO_3^- with OH^- , and indicate the conjugate acid–base pairs in each case. (b) A substance such as HCO_3^- that reacts with both H_3O^+ and OH^- is said to be _____. (Fill in the missing word.)
82. (a) List and name the conjugate bases of H_3PO_4 , NH_4^+ , and OH^- and the conjugate acids of HSO_4^- , PH_3 , and PO_4^{3-} . (b) Given that NO_2^- is a stronger base than NO_3^- , which is the stronger acid—nitric acid, HNO_3 , or nitrous acid, HNO_2 ?
83. A 0.1 M solution of copper(II) chloride, CuCl_2 , causes the light bulb in the conductivity experiment shown in Figure 6-1 to glow brightly. When hydrogen sulfide, H_2S , a very weak acid, is added to the solution, a black precipitate of copper(II) sulfide, CuS , forms, and the bulb still glows brightly. The experiment is repeated with a 0.1 M solution of copper(II) acetate, $\text{Cu}(\text{CH}_3\text{COO})_2$, which also causes the bulb to glow brightly. Again, CuS forms, but this time the bulb glows dimly. With the aid of ionic equations, explain the difference in behavior between the CuCl_2 and $\text{Cu}(\text{CH}_3\text{COO})_2$ solutions.



Charles D. Winters

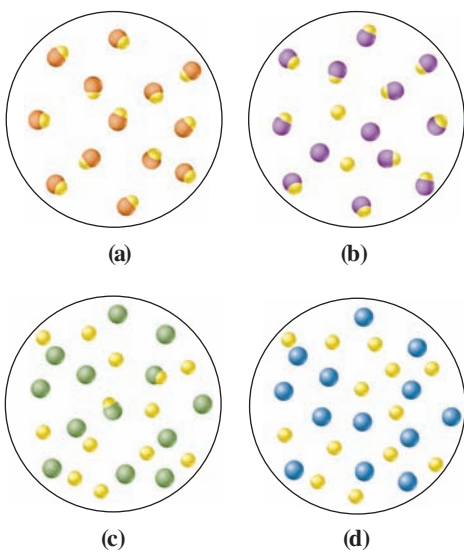
Conductivity experiment

84. Referring again to Figure 6-1, explain the following results of a conductivity experiment (use ionic equations).
(a) Individual solutions of NaOH and HCl cause the bulb to glow brightly. When the solutions are mixed, the bulb still glows brightly but not as brightly as before.
(b) Individual solutions of NH_3 and CH_3COOH cause the bulb to glow dimly. When the solutions are mixed, the bulb glows brightly.
85. When a 0.1 M aqueous ammonia solution is tested with a conductivity apparatus (see Figure 6-1), the bulb glows dimly. When a 0.1 M hydrochloric acid solution is

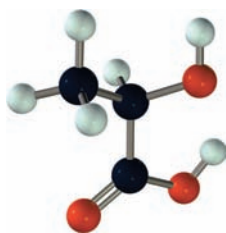
tested, the bulb glows brightly. Would you expect the bulb to glow more brightly, stop glowing, or stay the same as very pure water is added to each of the solutions? Explain your reasoning.

Conceptual Exercises

86. Distinguish between solubility in water and extent of ionization in water. Provide specific examples that illustrate the meanings of both terms.
87. Write three general statements that describe the extents to which acids, bases, and salts are ionized in dilute aqueous solutions.
88. The following diagrams are nanoscale representations of different acids in aqueous solution; the water molecules are not shown. The small yellow spheres are hydrogen atoms or ions. The larger spheres represent the anions.
- (a) Which diagram best represents hydrochloric acid?
- (b) Which diagram best represents hydrofluoric acid?



89. One of the chemical products of muscle contraction is lactic acid ($\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$), a monoprotic acid whose structure is



Prolonged exercise can temporarily overload the body's capacity for elimination of this substance, and the resulting increase in lactic acid concentration in the muscles causes pain and stiffness. (a) Lactic acid has six H atoms per molecule, yet it acts as a monoprotic acid in an aqueous

environment. Which of the H atoms is ionizable? (b) Draw the structural formula of the conjugate base. (c) Write a net ionic equation that illustrates the ionization of lactic acid in water. (d) Describe the geometry around each of the carbon atoms in lactic acid.



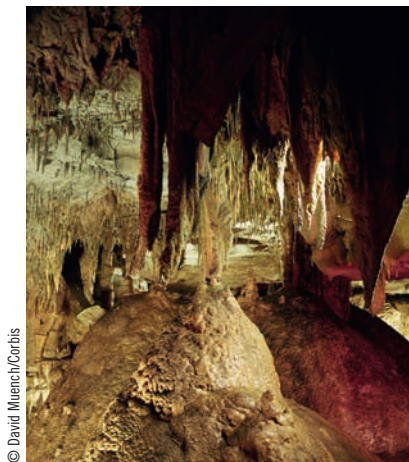
Runners experience lactic acid buildup.

90. On the planet Baseacidopolous, the major solvent is liquid ammonia, not water. Ammonia autoionizes much like water ($2\text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$). If instead of water, ammonia is used as a solvent: (a) What is the formula of the cation that would indicate that a compound is an acid? (b) What is the formula of the anion produced if a compound is a base? (c) Look at the way that NaCl is formed from an acid–base reaction on earth and determine if NaCl can be a salt on Baseacidopolous.
91. Some of the acid formed in tissues is excreted through the kidneys. One of the bases removing the acid is HPO_4^{2-} . Write the equation for the reaction. Could Cl^- serve this function?
92. Suppose 1 mole of hydrochloric acid, HCl, is dissolved in 1 liter of water. List the following species in order of decreasing concentration: HCl, H_2O , Cl^- , H_3O^+ .
93. Suppose 1 mole of acetic acid, CH_3COOH , is dissolved in 1 liter of water. List the following species in order of decreasing concentration: CH_3COOH , H_2O , H^+ , CH_3COO^- , H_3O^+ .
94. (a) Give an example of a substance that is an acid and one that is a base, according to the Arrhenius theory of acids and bases. (b) Give an example of a Brønsted-Lowry acid that is not an Arrhenius acid. (c) Give an example of a Brønsted-Lowry base that is not an Arrhenius base. (d) Can you give an example of an Arrhenius acid or base that is not a Brønsted-Lowry acid or base?
95. List the following ions in order of decreasing base strength: HO^- , HS^- , HSe^- , HTe^- .
96. Draw a Lewis formula for the base in each of the following Lewis acid–base reactions. What do all of the bases have in common?
- $$\text{I}_2 + \text{I}^- \longrightarrow \text{I}_3^-$$
- $$\text{Zn}^{2+} + 4\text{NH}_3 \longrightarrow [\text{Zn}(\text{NH}_3)_4]^{2+}$$
- $$2\text{F}^- + \text{SiF}_4 \longrightarrow [\text{SiF}_6]^{2-}$$
- $$\text{BH}_3 + \text{CO} \longrightarrow \text{H}_3\text{BCO}$$

97. Write the formula unit equations, the total ionic equations, and net ionic equations for the reactions of nitric acid, HNO_3 , with potassium hydroxide, KOH , and of carbonic acid, H_2CO_3 , with potassium hydroxide, KOH . What differences do you observe between the net ionic equation for the reaction of nitric acid, a strong acid, with a strong base and the net ionic equation for the reaction of carbonic acid, a weak acid, with a strong base?
98. Suppose one mole of hydrosulfuric acid, H_2S , reacts with one mole of sodium hydroxide: $\text{H}_2\text{S} + \text{NaOH} \longrightarrow \text{NaHS} + \text{H}_2\text{O}$. Then suppose that one mole of the product of this reaction reacts with one more mole of sodium hydroxide: $\text{NaHS} + \text{NaOH} \longrightarrow \text{Na}_2\text{S} + \text{H}_2\text{O}$. Classify each substance— H_2S , NaOH , NaHS , and Na_2S —as a strong acid, a strong base, a weak acid, a weak base, a normal salt, an acidic salt, or a basic salt.
99. Lead(II) hydroxide, $\text{Pb}(\text{OH})_2$, is an insoluble (or “sparingly soluble”) base. It cannot produce a strongly basic solution by dissolution in distilled water, but it does react with strong acids. It will also react with an excess of a strong base to produce plumbite, $[\text{Pb}(\text{OH})_4]^{2-}$, a complex ion. Explain the solubility of $\text{Pb}(\text{OH})_2$ in both strong acids and strong bases by writing the complete, balanced equations for the reactions of $\text{Pb}(\text{OH})_2$ with nitric acid, $\text{HNO}_3(\text{aq})$, and with potassium hydroxide, $\text{KOH}(\text{aq})$.

Building Your Knowledge

100. Autoionization can occur when an ion other than H^+ is transferred, as exemplified by the transfer of a Cl^- ion from one PCl_5 molecule to another. Write the equation for this reaction. What are the shapes of the two ions that are formed?
101. Limestone, CaCO_3 , is a water-insoluble material, whereas $\text{Ca}(\text{HCO}_3)_2$ is soluble. Caves are formed when rainwater containing dissolved CO_2 passes over limestone for long periods of time. Write a chemical equation for the acid–base reaction.



© David Muench/Corbis

Cave formation

102. Acids react with metal carbonates and hydrogen carbonates to form carbon dioxide and water. (a) Write the balanced equation for the reaction that occurs when baking soda, NaHCO_3 , and vinegar, 5% acetic acid, are mixed. What causes the “fizz”? (b) Lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, is found in sour milk and in buttermilk. Many of its reactions are very similar to those of acetic acid. Write the balanced equation for the reaction of baking soda, NaHCO_3 , with lactic acid. Explain why bread “rises” during the baking process.

Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

103. Use an internet search engine (such as <http://www.google.com>) to locate information on carbonated beverages known as colas. (a) What acid(s) is (are) present in a cola? (b) What is the molarity of the acids in the best known cola?
104. Go to a suitable site on the web, then search for Lewis acid–base theory and answer the following questions: What was the full name of the person that Lewis acid–base theory is named for? When did he propose the Lewis theory of acids and bases?
105. Go to www.almaz.com/nobel/chemistry or another suitable website. How old was Svante Arrhenius when he received the Nobel Prize? Who received the Nobel Prize in Chemistry in 2005? Briefly describe the work for which this prize was awarded (you might need to search elsewhere on the web).



Molecular Reasoning exercises



More Challenging exercises

Blue-Numbered exercises

solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

Reactions in Aqueous Solutions II: Calculations

11



Purple potassium permanganate (KMnO_4) is added to a solution of Fe^{2+} , oxidizing it to produce light yellow Fe^{3+} and colorless Mn^{2+} .

Charles D. Winters

OUTLINE

Aqueous Acid–Base Reactions

- 11-1 Calculations Involving Molarity
- 11-2 Titrations
- 11-3 Calculations for Acid–Base Titrations

Oxidation–Reduction Reactions

- 11-4 Balancing Redox Equations
- 11-5 Adding H^+ , OH^- , or H_2O to Balance Oxygen or Hydrogen
- 11-6 Calculations for Redox Titrations

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Perform molarity calculations
- ▶ Solve acid–base stoichiometry calculations
- ▶ Describe titration and standardization
- ▶ Carry out calculations for acid–base titrations
- ▶ Balance oxidation–reduction equations
- ▶ Carry out calculations for redox titrations

Aqueous Acid–Base Reactions

Hydrochloric acid, HCl, is sometimes called “stomach acid” because it is the main acid ($\approx 0.10\text{ M}$) in our digestive juices. When the concentration of HCl is too high in humans, problems result. These problems may range from “heartburn” to ulcers that can eat through the lining of the stomach wall. Snakes have very high concentrations of HCl in their digestive juices so that they can digest whole small animals and birds.

Automobile batteries contain 40% H_2SO_4 by mass. When the battery has “run down,” the concentration of H_2SO_4 is significantly lower than 40%. A technician checks an automobile battery by drawing some battery acid into a hydrometer, which indicates the density of the solution. This density is related to the concentration of H_2SO_4 , which is more dense than water.

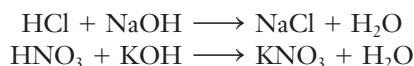
There are many practical applications of acid–base chemistry in which we must know the concentration of a solution of an acid or a base.

11-1 Calculations Involving Molarity

▶ Digestive juice is the acidic fluid secreted by glands in the lining of the stomach.

In Sections 3-6 through 3-8 we introduced methods for expressing concentrations of solutions and discussed some related calculations. Review of those sections will be helpful as we learn more about acid–base reactions in solutions.

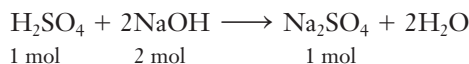
The *reaction ratio* (see Section 3-2) is the relative number of moles of reactants and products shown in the balanced equation. In many cases, one mole of an acid reacts with one mole of a base to yield neutralization.



These acids have only one acidic hydrogen per formula unit, and these bases have only one hydroxide ion per formula unit, so one formula unit of base reacts with one formula unit of acid. Thus, one mole of each acid reacts with one mole of each base in these cases, so the reaction ratio is

$$\frac{1 \text{ mol acid}}{1 \text{ mol base}} \quad \text{or} \quad \frac{1 \text{ mol base}}{1 \text{ mol acid}}$$

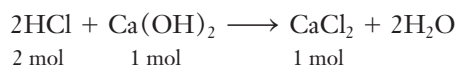
In other cases, however, more than one mole of a base is required to neutralize completely one mole of an acid, or more than one mole of an acid is required to neutralize completely one mole of a base. The balanced equation



shows that one mole of H_2SO_4 reacts with two moles of NaOH, so the reaction ratio is written as

$$\frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol NaOH}} \quad \text{or} \quad \frac{2 \text{ mol NaOH}}{1 \text{ mol H}_2\text{SO}_4}$$

The balanced equation



▶ Chemists sometimes use the term *equivalents* instead of moles when referring to reaction ratios. This is because a mole is a specific amount of material, while the term “equivalents” focuses on the relative amounts of materials that react with one another, as shown by the coefficients of the balanced chemical equation.

Unless otherwise noted, all content on this page is © Cengage Learning.

tells us that two moles of HCl react with one mole of $\text{Ca}(\text{OH})_2$, so the reaction ratio is

$$\frac{2 \text{ mol HCl}}{1 \text{ mol Ca}(\text{OH})_2} \quad \text{or} \quad \frac{1 \text{ mol Ca}(\text{OH})_2}{2 \text{ mol HCl}}$$

As with all reaction stoichiometry calculations (see Chapter 3), you must pay close attention to the balanced equation and the resulting reaction ratio in all examples and problems in this chapter. The next several examples illustrate such calculations.

EXAMPLE 11-1 Acid–Base Reactions

If 100. mL of 0.100 M HCl solution and 100. mL of 0.100 M NaOH are mixed, what is the molarity of the salt in the resulting solution? Assume that the volumes are additive.

Plan

We first write the balanced equation for the acid–base reaction and then construct the reaction summary that shows the amounts (moles) of HCl and NaOH. We determine the amount of salt formed from the reaction summary by multiplying the volume times the molarity. Remember that you cannot directly add or subtract molarities, only moles (or mmoles). The final (total) volume is the sum of the volumes mixed. Then we calculate the molarity of the salt.

Solution

The following tabulation, called the *reaction summary*, shows that equal numbers of moles of HCl and NaOH are mixed and, therefore, all of the HCl and NaOH react. The resulting solution contains only NaCl, the salt formed by the reaction, and water (the amount of water produced in this reaction is negligible since the reaction takes place in water).

	HCl	+	NaOH	→	NaCl + H ₂ O
Rxn ratio:	1 mol		1 mol		1 mol 1 mol
Start:	$\left[0.100 \text{ L} \left(\frac{0.100 \text{ mol}}{\text{L}}\right)\right]$		$\left[0.100 \text{ L} \left(\frac{0.100 \text{ mol}}{\text{L}}\right)\right]$		0 mol
	0.0100 mol HCl		0.0100 mol NaOH		
Change:	−0.0100 mol		−0.0100 mol		+ 0.0100 mol
After rxn:	0 mol		0 mol		0.0100 mol

The HCl and NaOH neutralize each other exactly, and the resulting solution contains 0.0100 mol of NaCl in 0.200 L of solution. Its molarity is

$$\frac{? \text{ mol NaCl}}{\text{L}} = \frac{0.0100 \text{ mol NaCl}}{0.200 \text{ L}} = 0.0500 \text{ M NaCl}$$

We can check the result of this simple example qualitatively by considering that we doubled the total volume of the solution, which represents a dilution of all the species in solution. This reduces the concentration of all the species in solution by a factor of two.

► Experiments have shown that volumes of *dilute* aqueous solutions are very nearly additive. No significant error is introduced by making this assumption. 0.100 L of dilute NaOH solution mixed with 0.100 L of dilute HCl solution gives 0.200 L of solution.

STOP & THINK

Remember that the balanced equation shows the relative number of moles of each reactant and product involved in the reaction. Review the definition of molarity and uses of molarity (see Sections 3-6 and 3-8).

STOP & THINK

The most common mistake in working out this type of problem is forgetting to use the combined solution volume when calculating the final concentration.

We often express the volume of a solution in milliliters rather than in liters. Likewise, we may express the amount of solute in millimoles (mmol) rather than in moles. Because one milliliter is 1/1000 of a liter and one **millimole** is 1/1000 of a mole, molarity also may be expressed as the number of millimoles of solute per milliliter of solution:

$$\text{molarity} = \frac{\text{number of millimoles of solute}}{\text{number of milliliters of solution}}$$

$$\begin{aligned} 1 \text{ mol} &= 1000 \text{ mmol} \\ 1 \text{ L} &= 1000 \text{ mL} \\ \text{molarity} &= \frac{\text{no. mol}}{\text{L}} = \frac{\text{no. mmol}}{\text{mL}} \end{aligned}$$

For volumes and concentrations that are commonly used in laboratory experiments, solving problems in terms of millimoles and milliliters often involves more convenient num-

STOP & THINK

You cannot mix mmols and mL with moles and L (liters). If you use mmols you must also use volumes in mL.

bers than using moles and liters. We should note also that the reaction ratio that we obtain from any balanced chemical equation is the same whether we express all quantities in moles or in millimoles. We will work many problems in this chapter using millimoles and milliliters. Let us see how we might solve Example 11-1 in these terms.

As in Example 11-1 we first write the balanced equation for the acid–base reaction, and then construct the reaction summary that shows the amounts (millimoles) of NaOH and HCl. We determine the amount of salt formed from the reaction summary. The final (total) volume is the sum of the volumes mixed. Then we can calculate the molarity of the salt.

The tabulation for the solution is

	HCl	+	NaOH	→	NaCl + H ₂ O
Rxn ratio:	1 mmol		1 mmol		1 mmol 1 mmol
Start:	$\left[100. \text{ mL} \left(\frac{0.100 \text{ mmol}}{\text{mL}} \right)\right]$		$\left[100. \text{ mL} \left(\frac{0.100 \text{ mmol}}{\text{mL}} \right)\right]$		0 mmol
	= 10.0 mmol HCl		= 10.0 mmol NaOH		
Change:	−10.0 mmol		−10.0 mmol		+ 10.0 mmol
After rxn:	0 mmol		0 mmol		10.0 mmol
	$\frac{? \text{ mmol NaCl}}{\text{mL}} = \frac{10.0 \text{ mmol NaCl}}{200. \text{ mL}} = 0.0500 \text{ M NaCl}$				

EXAMPLE 11-2 Acid–Base Reactions

If 100. mL of 1.00 M HCl and 100. mL of 0.80 M NaOH solutions are mixed, what are the molarities of the solutes in the resulting solution?

Plan

We proceed as we did in Example 11-1. This reaction summary shows that NaOH is the limiting reactant and that we have excess HCl.

Solution

	HCl	+	NaOH	→	NaCl	+	H ₂ O
Rxn ratio:	1 mmol		1 mmol		1 mmol		1 mmol
Start:	100. mmol		80. mmol		0 mmol		
Change:	−80. mmol		−80. mmol		+80. mmol		
After rxn:	20. mmol		0 mmol		80. mmol		

Because two solutes are present in the solution after reaction, we must calculate the concentrations of both.

$$\frac{? \text{ mmol HCl}}{\text{mL}} = \frac{20. \text{ mmol HCl}}{200. \text{ mL}} = 0.10 \text{ M HCl}$$

$$\frac{? \text{ mmol NaCl}}{\text{mL}} = \frac{80. \text{ mmol NaCl}}{200. \text{ mL}} = 0.40 \text{ M HCl}$$

Both HCl and NaCl are strong electrolytes, so the solution is 0.10 M in H⁺ (aq), (0.10 + 0.40) M = 0.50 M in Cl[−], and 0.40 M in Na⁺ ions.

You should now work Exercise 14.

STOP & THINK

You should master these initial examples before attempting the following more complex ones.

Problem-Solving Tip Review Limiting Reactant Calculations

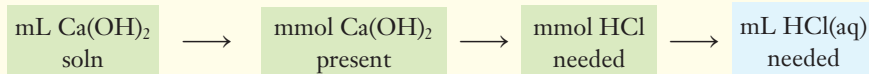
To solve many of the problems in this chapter, you will need to apply the limiting reactant concept (see Section 3-3). In Example 11-1, we confirm that the two reactants are initially present in the mole ratio required by the balanced chemical equation; they both react completely, so there is no excess of either one. In Example 11-2, we need to determine which reactant limits the reaction. Before you proceed, be sure you understand how the ideas of Section 3-3 are used in these examples.

EXAMPLE 11-3 Volume of Acid to Neutralize Base

What volume of 0.00300 M HCl solution would just neutralize 30.0 mL of 0.00100 M Ca(OH)₂ solution?

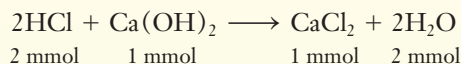
Plan

We write the balanced equation for the reaction to determine the reaction ratio. Then we (1) convert milliliters of Ca(OH)₂ solution to millimoles of Ca(OH)₂ using molarity in the reaction ratio, 0.00100 mmol Ca(OH)₂/1.00 mL Ca(OH)₂ solution; (2) convert millimoles of Ca(OH)₂ to millimoles of HCl using the reaction ratio, 2 mmol HCl/1 mmol Ca(OH)₂ (from the balanced equation); and (3) convert millimoles of HCl to milliliters of HCl solution using the ratio, 1.00 mL HCl/0.00300 mmol HCl, that is, molarity inverted.



Solution

The balanced equation for the reaction is



? mL HCl =

$$\begin{aligned}
 30.0 \text{ mL Ca(OH)}_2 &\times \frac{0.00100 \text{ mmol Ca(OH)}_2}{1.00 \text{ mL Ca(OH)}_2} \times \frac{2 \text{ mmol HCl}}{1 \text{ mmol Ca(OH)}_2} \times \frac{1.00 \text{ mL HCl}}{0.00300 \text{ mmol HCl}} \\
 &= 20.0 \text{ mL HCl}
 \end{aligned}$$

You should now work Exercise 24.

STOP & THINK

Students often mistakenly try to use the relation

$$V_1 M_1 = V_2 M_2$$

to solve problems about solution stoichiometry.

This equation is intended *only* for dilution problems and should never be used for problems involving reactions.

► The balanced chemical equation allows us to construct the reaction ratio as either a mole ratio or a millimole ratio.

$$\frac{2 \text{ mol HCl}}{1 \text{ mol Ca(OH)}_2} \quad \text{or}$$

$$\frac{2 \text{ mmol HCl}}{1 \text{ mmol Ca(OH)}_2}$$

We must always write the balanced equation and determine the *reaction ratio*. In Example 11-3, the balanced equation shows that two moles of HCl is required to neutralize one mole of Ca(OH)₂. We use the reaction ratio 2 mol HCl/1 mol Ca(OH)₂ to convert moles of Ca(OH)₂ to moles of HCl.

Problem-Solving Tip There Is More Than One Way to Solve Some Problems

In many problems more than one “plan” can be followed. In Example 11-3 a particular plan was used successfully. Many students can more easily visualize the solution by following a plan such as that in Examples 11-1 and 11-4. We suggest that you use the plan that you find most understandable.

EXAMPLE 11-4 Acid–Base Reactions

If 100. mL of 1.00 M H_2SO_4 solution is mixed with 200. mL of 1.00 M KOH , what salt is produced, and what is its molarity?

Plan

We proceed as we did in Example 11-2. We note that the reaction ratio is 1 mmol of H_2SO_4 to 2 mmol of KOH to 1 mmol of K_2SO_4 .

Solution

	H_2SO_4	+	2KOH	$\longrightarrow$	K_2SO_4	+	$2\text{H}_2\text{O}$
Rxn ratio:	1 mmol		2 mmol		1 mmol		
Start:	$\left[100. \text{ mL} \left(\frac{1.00 \text{ mmol}}{\text{mL}}\right)\right]$		$\left[200. \text{ mL} \left(\frac{1.00 \text{ mmol}}{\text{mL}}\right)\right]$				
	= 100. mmol		= 200. mmol		0 mmol		
Change:	–100. mmol		–200. mmol		+100. mmol		
After rxn:	0 mmol		0 mmol		100. mmol		

The reaction produces 100. mmol of potassium sulfate. This is contained in 300. mL of solution, so the concentration is

$$\frac{? \text{ mmol } \text{K}_2\text{SO}_4}{\text{mL}} = \frac{100. \text{ mmol } \text{K}_2\text{SO}_4}{300. \text{ mL}} = 0.333 \text{ M } \text{K}_2\text{SO}_4$$

You should now work Exercise 12.

STOP & THINK

Don't forget to add the individual solution volumes to find the volume of the final solution.

► Because K_2SO_4 is a soluble salt, this corresponds to 0.666 M K^+ and 0.333 M SO_4^{2-} .

11-2 Titrations

In Examples 3-24 and 11-3, we calculated the volume of one solution that is required to react with a given volume of another solution, with the concentrations of *both* solutions given. In the laboratory we often measure the volume of one solution that is required to react with a given volume of another solution, where only one concentration is known. Then we calculate the concentration of the other solution. This procedure is called *titration* (Figure 11-1).

Titration is the procedure in which a solution of one reactant, the titrant, is carefully added to a solution of another reactant, and the volume of titrant required for complete reaction is measured. The concentration of one solution, usually (but not necessarily) the titrant, is known; this allows one to calculate the concentration or the amount of reactant in the other (unknown) solution, using the known reaction ratio.

How does one know when to stop a titration—that is, when is the chemical reaction just complete? In one method, a few drops of an indicator solution are added to the solution to be titrated. An acid–base **indicator** is a substance that can exist in different forms, with different colors that depend on the concentration of H^+ in the solution. At least one of these forms must be very intensely colored so that even very small amounts of it can be seen.

We can titrate an acid solution of unknown concentration by adding a standardized solution of sodium hydroxide dropwise from a **buret** (see Figure 11-1). A common buret is graduated in large intervals of 1 mL and in smaller intervals of 0.1 mL so that it is possible to estimate the volume of a solution dispensed to within at least ± 0.02 mL. (Experienced individuals can often read a buret to ± 0.01 mL.) The analyst tries to choose an indicator that changes color clearly at the point at which stoichiometrically equivalent amounts of acid and base have reacted, the **equivalence point**. The point at which the indicator changes color and the titration is stopped is called the **end point**. Ideally, the end point

► The choice of indicators will be discussed in Section 19-4.

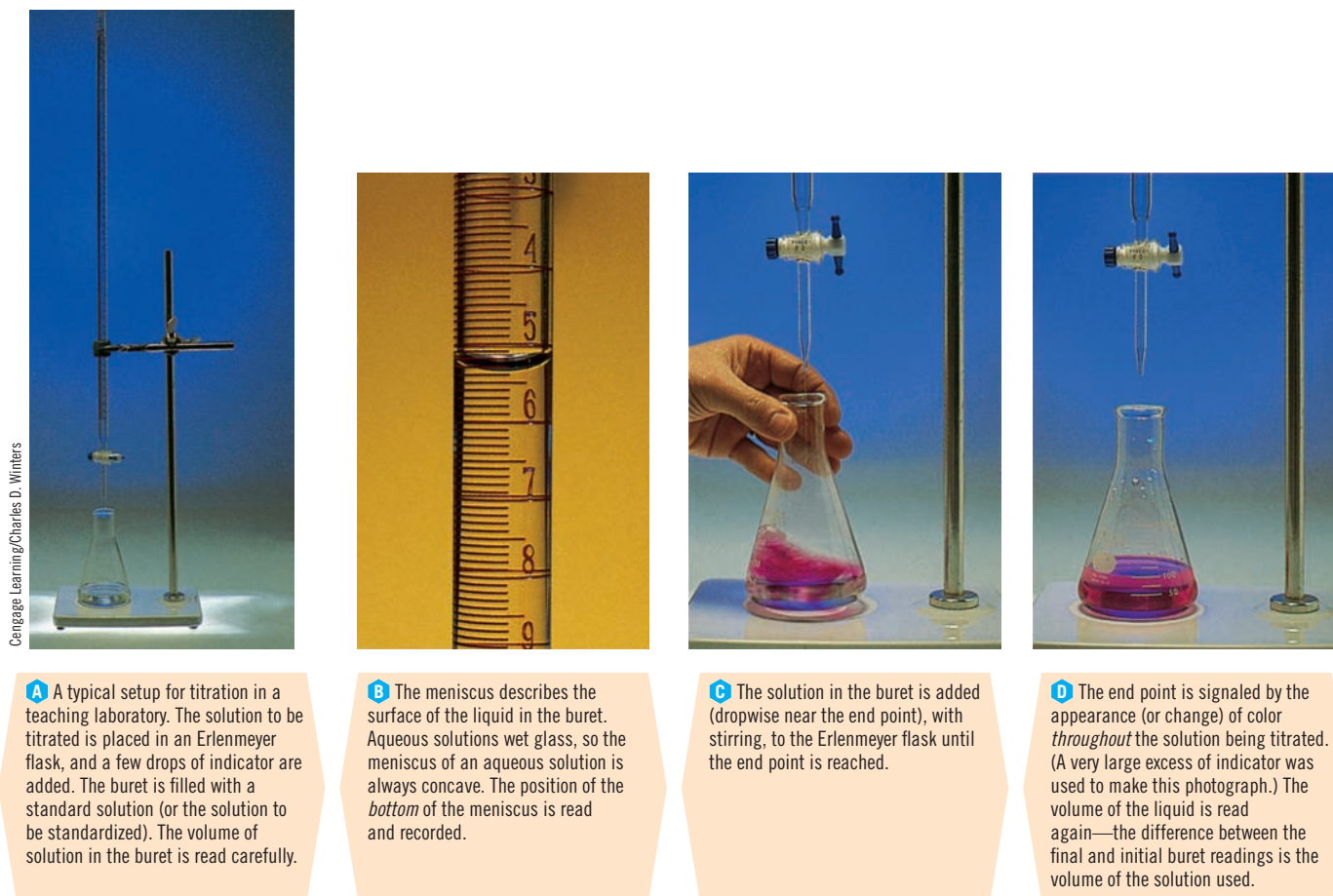


Figure 11-1 The titration procedure.

should coincide with the equivalence point. Phenolphthalein is colorless in acidic solution and reddish violet in basic solution. In a titration in which a base is added to an acid, phenolphthalein is often used as an indicator. The end point is signaled by the first appearance of a faint pink coloration that persists for at least 15 seconds as the solution is swirled.

Solutions with accurately known concentrations are called **standard solutions**. Often we prepare a solution of a substance and then determine its concentration by titration with a standard solution.

Standardization is the process by which one determines the concentration of a solution by measuring accurately the volume of the solution required to react with an accurately known amount of a **primary standard**. The standardized solution is then known as a **secondary standard** and is used in the analysis of unknowns.

The properties of an ideal *primary standard* include the following:

1. It must not react with or absorb the components of the atmosphere, such as water vapor, oxygen, and carbon dioxide.
2. It must react according to one invariable reaction.
3. It must have a high percentage purity.
4. It should have a high formula weight to minimize the effect of error in weighing.
5. It must be soluble in the solvent of interest.
6. It should be nontoxic.
7. It should be readily available (inexpensive).
8. It should be environmentally friendly.

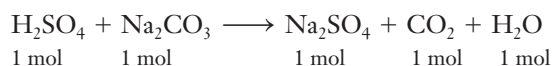
► CO_2 , H_2O , and O_2 are present in the atmosphere. They react with many substances. In particular, CO_2 gradually reacts with hydroxide bases to neutralize the base. Thus, it is particularly important to use freshly standardized hydroxide solutions in titrations.

The first five of these characteristics are essential to minimize the errors involved in analytical methods. The last three characteristics are just as important as the first five in most analytical laboratories. Because primary standards are often costly and difficult to prepare, secondary standards are often used in day-to-day work.

11-3 Calculations for Acid–Base Titrations

An **acid–base titration** is the quantitative analysis of the amount or concentration of an acid or base in a sample by observing its reaction with a known amount or concentration of a base or acid.

Let us now describe the use of a few primary standards for acids and bases. One primary standard for solutions of acids is sodium carbonate, Na_2CO_3 , a solid compound.



$$1 \text{ mol Na}_2\text{CO}_3 = 106.0 \text{ g} \quad \text{and} \quad 1 \text{ mmol Na}_2\text{CO}_3 = 0.1060 \text{ g}$$

► Review the Brønsted–Lowry theory (see Section 10-4).

Sodium carbonate is a salt. Because a base can be broadly defined as a substance that reacts with hydrogen ions, in *this* reaction Na_2CO_3 can be thought of as a base.



Sodium carbonate is often used as a primary standard for acids.

STOP & THINK

We use the definition of the mole, the reaction ratio, and the definition of molarity to write the three unit factors used in this example.

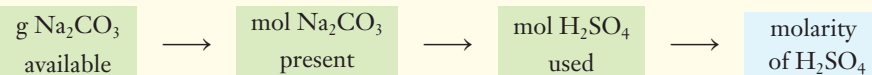
► The “ph” in *phthalate* is silent. Phthalate is pronounced “thalate.”

EXAMPLE 11-5 Standardization of an Acid Solution

Calculate the molarity of a solution of H_2SO_4 if 40.0 mL of the solution neutralizes 0.364 g of Na_2CO_3 .

Plan

We know from the balanced equation that 1 mol of H_2SO_4 reacts with 1 mol of Na_2CO_3 , 106.0 g. This provides the reaction ratio that converts 0.364 g of Na_2CO_3 to the corresponding number of moles of H_2SO_4 , from which we can calculate molarity.



Solution

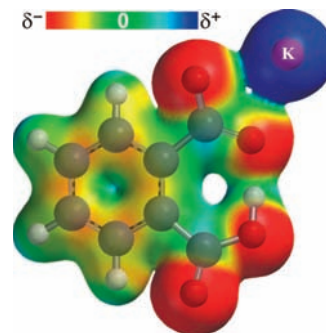
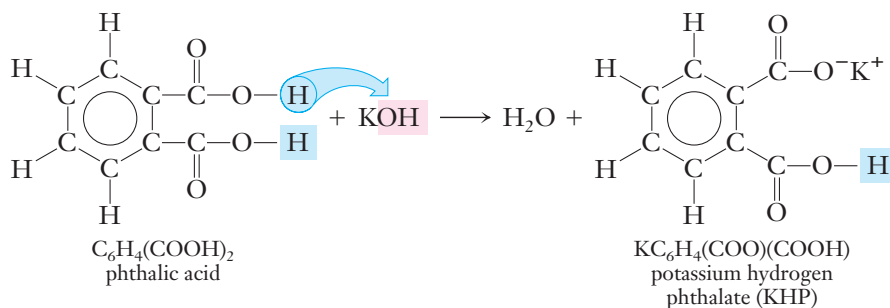
$$\begin{aligned} \underline{\hspace{1cm}} \text{ mol H}_2\text{SO}_4 &= 0.364 \text{ g Na}_2\text{CO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{106.0 \text{ g Na}_2\text{CO}_3} \times \frac{1 \text{ mol H}_2\text{SO}_4}{1 \text{ mol Na}_2\text{CO}_3} \\ &= 0.00343 \text{ mol H}_2\text{SO}_4 \quad (\text{present in 40.0 mL of solution}) \end{aligned}$$

Now we calculate the molarity of the H_2SO_4 solution

$$\frac{\underline{\hspace{1cm}} \text{ mol H}_2\text{SO}_4}{\text{L}} = \frac{0.00343 \text{ mol H}_2\text{SO}_4}{0.0400 \text{ L}} = 0.0858 \text{ M H}_2\text{SO}_4$$

You should now work Exercise 26.

Most inorganic bases are metal hydroxides, all of which are solids. Even in the solid state, however, most inorganic bases react rapidly with CO_2 (an acid anhydride) from the atmosphere. Most metal hydroxides also absorb H_2O from the air. These properties make it *very* difficult to weigh out samples of pure metal hydroxides accurately. Chemists obtain solutions of bases of accurately known concentration by standardizing the solutions against an acidic salt, potassium hydrogen phthalate, $\text{KC}_6\text{H}_4(\text{COO})(\text{COOH})$. This is produced by neutralization of one of the two ionizable hydrogens of an organic acid, phthalic acid.



The P in KHP stands for the phthalate ion, $\text{C}_6\text{H}_4(\text{COO})_2^{2-}$, not phosphorus.

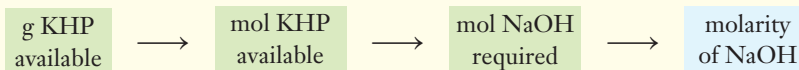
This acidic salt, known simply as KHP, has one remaining acidic hydrogen (highlighted) that reacts with bases. KHP is easily obtained in a high state of purity and is soluble in water. It is used as a primary standard for bases.

EXAMPLE 11-6 Standardization of Base Solution

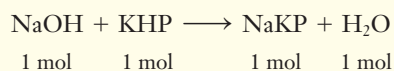
A 20.00-mL sample of a solution of NaOH reacts with 0.3641 g of KHP. Calculate the molarity of the NaOH solution.

Plan

We first write the balanced equation for the reaction between NaOH and KHP. We then calculate the number of moles of NaOH in 20.00 mL of solution from the amount of KHP that reacts with it. Then we can calculate the molarity of the NaOH solution.



Solution



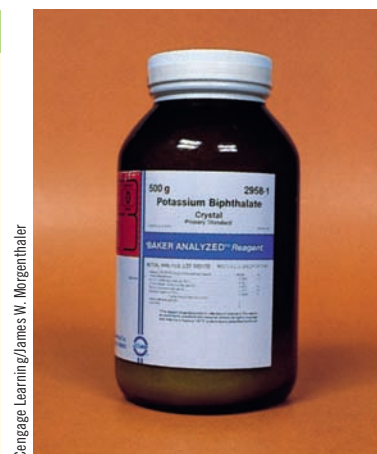
We see that NaOH and KHP react in a 1:1 reaction ratio. One mole of KHP is 204.2 g.

$$\underline{\hspace{1cm}} \text{ mol NaOH} = 0.3641 \text{ g KHP} \times \frac{1 \text{ mol KHP}}{204.2 \text{ g KHP}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol KHP}} = 0.001783 \text{ mol NaOH}$$

Then we calculate the molarity of the NaOH solution.

$$\frac{\underline{\hspace{1cm}} \text{ mol NaOH}}{\text{L}} = \frac{0.001783 \text{ mol NaOH}}{0.02000 \text{ L}} = 0.08915 \text{ M NaOH}$$

You should now work Exercise 28.



Cengage Learning/James W. Morgenthaier

Very pure KHP is readily available.

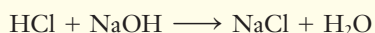
STOP & THINK

The use of unit factors helps us set up the solution to this problem.

The concentration of an acid solution can be determined by titration with a standard solution of a base, as illustrated by the following two examples.

EXAMPLE 11-7 Titration

The titration of 36.7 mL of a hydrochloric acid solution requires 43.2 mL of standard 0.236 M sodium hydroxide solution for complete neutralization. What is the molarity of the HCl solution?



STOP & THINK

Remember!

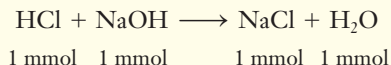
$$\text{molarity} = \frac{\text{mmol of solute}}{\text{mL of solution}}$$

STOP & THINK

Unit factors lead to the appropriate units of the answer (M HCl). The equation shows that equal numbers of moles of HCl and NaOH react, and the volumes of the two solutions are similar. Thus it is reasonable that the answer ($0.278 M$ HCl) is similar to the given molarity of the standard NaOH solution.

Plan

The balanced equation tells us that the reaction ratio is one millimole of HCl to one millimole of NaOH, which gives the conversion factor, 1 mmol HCl/1 mmol NaOH.



First we find the number of millimoles of NaOH. The reaction ratio is one millimole of HCl to one millimole of NaOH, so the HCl solution must contain the same number of millimoles of HCl. Then we can calculate the molarity of the HCl solution because we know its volume.

$$\text{vol, } M \text{ of NaOH soln} \longrightarrow \text{mmol NaOH} \longrightarrow \text{mmol HCl} \longrightarrow M \text{ HCl soln}$$

Solution

The volume of a solution (in milliliters) multiplied by its molarity gives the number of millimoles of solute.

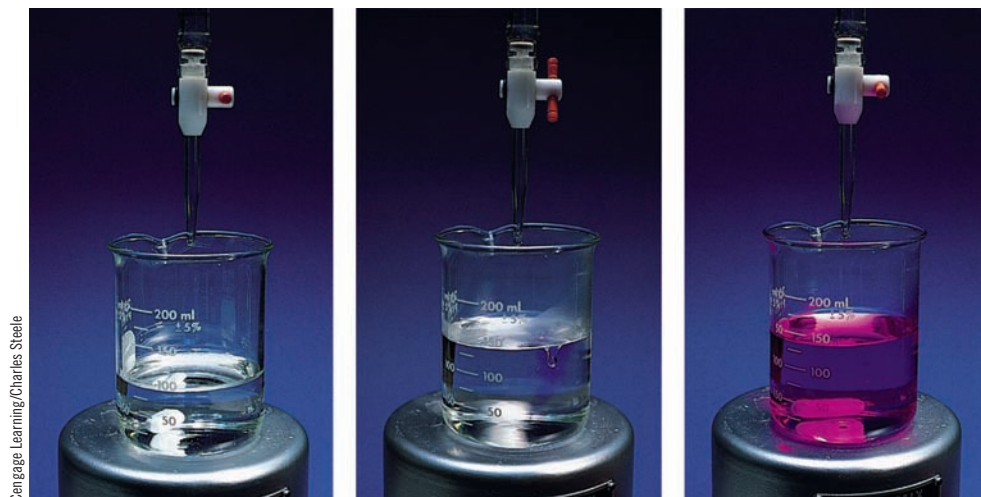
$$\underline{\hspace{1cm}} \text{ mmol NaOH} = 43.2 \text{ mL NaOH soln} \times \frac{0.236 \text{ mmol NaOH}}{1 \text{ mL NaOH soln}} = 10.2 \text{ mmol NaOH}$$

Because the reaction ratio is one millimole of NaOH to one millimole of HCl, the HCl solution must contain 10.2 millimole HCl.

$$\underline{\hspace{1cm}} \text{ mmol HCl} = 10.2 \text{ mmol NaOH} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol NaOH}} = 10.2 \text{ mmol HCl}$$

We know the volume of the HCl solution, so we can calculate its molarity.

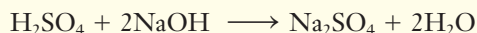
$$\frac{\underline{\hspace{1cm}} \text{ mmol HCl}}{\text{mL HCl soln}} = \frac{10.2 \text{ mmol HCl}}{36.7 \text{ mL HCl soln}} = 0.278 M \text{ HCl}$$



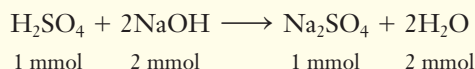
A base solution is added from the buret to the acid solution in the beaker. The indicator phenolphthalein changes from colorless, its color in acidic solutions, to pink, its color in basic solutions, when the reaction reaches completion. Note the first appearance of a faint pink coloration in the middle beaker; this signals that the end point is near.

EXAMPLE 11-8 Titration

The titration of 36.7 mL of a sulfuric acid solution requires 43.2 mL of standard 0.236 M sodium hydroxide solution for complete neutralization. What is the molarity of the H_2SO_4 solution?

**Plan**

The balanced equation tells us that the reaction ratio is one millimole of H_2SO_4 to two millimoles of NaOH, which gives the conversion factor, 1 mmol H_2SO_4 /2 mmol NaOH.



First we find the number of millimoles of NaOH. The reaction ratio is one millimole of H_2SO_4 to two millimoles of NaOH, so the number of millimoles of H_2SO_4 must be one half of the number of millimoles of NaOH. Then we can calculate the molarity of the H_2SO_4 solution because we know its volume.

**Solution**

The volume of a solution (in milliliters) multiplied by its molarity gives the number of millimoles of solute.

$$\underline{\hspace{1cm}} \text{ mmol NaOH} = 43.2 \text{ mL NaOH soln} \times \frac{0.236 \text{ mmol NaOH}}{1 \text{ mL NaOH soln}} = 10.2 \text{ mmol NaOH}$$

Because the reaction ratio is two millimoles of NaOH to one millimole of H_2SO_4 , the H_2SO_4 solution must contain 5.10 millimoles of H_2SO_4 .

$$\underline{\hspace{1cm}} \text{ mmol H}_2\text{SO}_4 = 10.2 \text{ mmol NaOH} \times \frac{1 \text{ mmol H}_2\text{SO}_4}{2 \text{ mmol NaOH}} = 5.10 \text{ mmol H}_2\text{SO}_4$$

We know the volume of the H_2SO_4 solution, so we can calculate its molarity.

$$\frac{\underline{\hspace{1cm}} \text{ mmol H}_2\text{SO}_4}{\text{mL H}_2\text{SO}_4 \text{ soln}} = \frac{5.10 \text{ mmol H}_2\text{SO}_4}{36.7 \text{ mL H}_2\text{SO}_4 \text{ soln}} = 0.139 M \text{ H}_2\text{SO}_4$$

You should now work Exercise 38.

STOP & THINK

Notice the similarity between Examples 11-7 and 11-8 in which the same volumes and molarities are used. In Example 11-7 the reaction ratio is 1 mmol acid/1 mmol base, whereas in Example 11-8 the reaction ratio is 1 mmol acid/2 mmol base, so the molarity of the HCl solution (0.278 M) is twice the molarity of the H_2SO_4 solution (0.139 M).

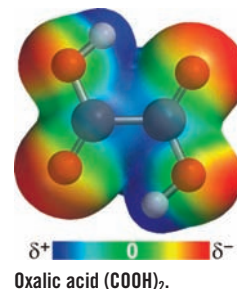
Impure samples of acids can be titrated with standard solutions of bases. The results can be used to determine percentage purity of the samples.

EXAMPLE 11-9 Determination of Percent Acid

Oxalic acid, $(\text{COOH})_2$, is used to remove rust stains and some ink stains from fabrics. A 0.1743-g sample of *impure* oxalic acid required 39.82 mL of 0.08915 M NaOH solution for complete neutralization. No acidic impurities were present. Calculate the percentage purity of the $(\text{COOH})_2$.

Plan

We write the balanced equation for the reaction and calculate the number of moles of NaOH in the standard solution. Then we calculate the mass of $(\text{COOH})_2$ in the sample, which gives us the information we need to calculate percentage purity.



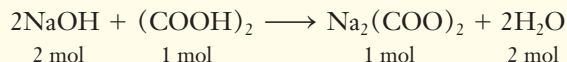
► Each molecule of $(\text{COOH})_2$ contains two acidic H's.

TOP & THINK

Again, we use carefully written unit factors from the stated molarity of $(\text{COOH})_2$, the reaction ratio, the formula weight of $(\text{COOH})_2$, and the definition of percentage to solve this problem. The percentage is reasonable (less than 100%).

Solution

The equation for the complete neutralization of $(\text{COOH})_2$ with NaOH is



Two moles of NaOH neutralizes completely one mole of $(\text{COOH})_2$. The number of moles of NaOH that react is the volume times the molarity of the solution.

$$\underline{} \text{ mol NaOH} = 0.03982 \text{ L} \times \frac{0.08915 \text{ mol NaOH}}{\text{L}} = 0.003550 \text{ mol NaOH}$$

Now we calculate the mass of $(\text{COOH})_2$ that reacts with 0.003550 mol NaOH.

$$\begin{aligned} \underline{} \text{ g } (\text{COOH})_2 &= 0.003550 \text{ mol NaOH} \times \frac{1 \text{ mol } (\text{COOH})_2}{2 \text{ mol NaOH}} \times \frac{90.04 \text{ g } (\text{COOH})_2}{1 \text{ mol } (\text{COOH})_2} \\ &= 0.1598 \text{ g } (\text{COOH})_2 \end{aligned}$$

The 0.1743-g sample contained 0.1598 g of $(\text{COOH})_2$, so its percentage purity was

$$\% \text{ purity} = \frac{0.1598 \text{ g } (\text{COOH})_2}{0.1743 \text{ g sample}} \times 100\% = 91.68\% \text{ pure } (\text{COOH})_2$$

You should now work Exercise 34.

Some chemists perform acid–base calculations using equivalent weights. In acid–base reactions, the mass of the acid (expressed in grams) that could furnish 6.022×10^{23} hydrogen ions (1 mol) or that could react with 6.022×10^{23} hydroxide ions (1 mol) is defined as one *equivalent weight* of the acid. Similarly, the mass of the base (expressed in grams) that could furnish 6.022×10^{23} hydroxide ions (1 mol) or that could react with 6.022×10^{23} hydrogen ions (1 mol) is defined as one *equivalent weight* of the base. The results of such calculations are always identical to those of the mole method we have used.

Oxidation–Reduction Reactions

In any balanced redox equation, the total increase in oxidation numbers must equal the total decrease in oxidation numbers. Our procedures for balancing redox equations are constructed to make sure this equivalence results. Many redox equations can be balanced by simple inspection, but you should master the systematic method presented here so that you can use it to balance difficult equations.

All balanced equations must satisfy two criteria.

1. There must be mass balance. That is, the same number of atoms of each kind must appear in reactants and products.
2. There must be charge balance. The sums of actual charges on the left and right sides of the equation must equal each other. In a balanced *formula unit equation*, the total charge on each side will be equal to zero. In a balanced *net ionic equation*, the total charge on each side might not be zero, but it still must be equal on the two sides of the equation.

11-4 Balancing Redox Equations

To balance a redox equation, we separate and completely balance equations describing oxidation and reduction **half-reactions**. Then we equalize the numbers of electrons gained and lost in each. Finally, we add the resulting half-reactions to give the overall balanced equation. The general procedure follows.

1. Write as much of the overall unbalanced equation as possible, omitting spectator ions.
2. Construct unbalanced oxidation and reduction half-reactions (these are usually incomplete as well as unbalanced). Show complete formulas for polyatomic ions and molecules. Tabulating the oxidation states can help you identify the oxidation and reduction half-reactions.
3. Balance by inspection all elements in each half-reaction, except H and O. Then use the chart in Section 11-5 to balance H and O in each half-reaction.
4. Balance the charge in each half-reaction by adding electrons as “products” or “reactants.”
5. Balance the electron transfer by multiplying the balanced half-reactions by appropriate integers.
6. Add the resulting half-reactions and eliminate any common terms.
7. Add common species that appear on the same side of the equation, and cancel equal amounts of common species that appear on opposite sides of the equation in equal amounts. The electrons must *always* cancel.
8. Check for mass balance (same number of atoms of each kind as reactants and products); check for charge balance (same total charge on both sides of the equation).

► The balancing procedure presented here is called the half-reaction method. Half-reactions are used extensively in electrochemistry (see Chapter 21).

STOP & THINK

If the electrons do not cancel in Step 7, go back and find your error in earlier steps. Students sometimes submit incorrect answers that they could easily avoid if they carefully checked the element balance and charge balance.

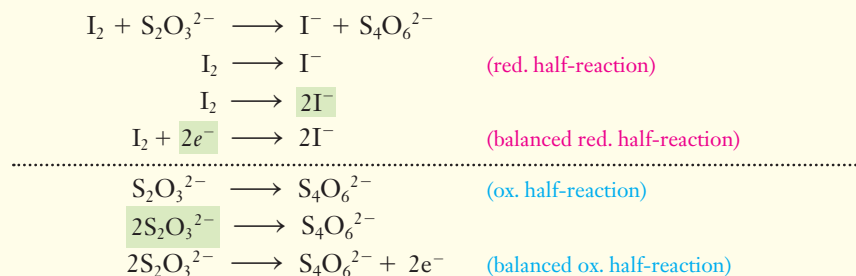
EXAMPLE 11-10 Balancing Redox Equations

A useful analytical procedure involves the oxidation of iodide ions to free iodine. The free iodine is then titrated with a standard solution of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$. Iodine oxidizes $\text{S}_2\text{O}_3^{2-}$ ions to tetrathionate ions, $\text{S}_4\text{O}_6^{2-}$, and is reduced to I^- ions. Write the balanced net ionic equation for this reaction.

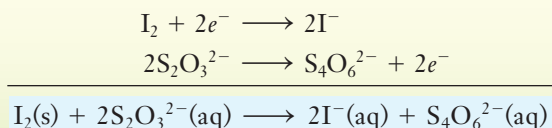
Plan

We are given the formulas for two reactants and two products. We use these to write as much of the equations as possible. We construct and balance the appropriate half-reactions using the rules just described. Then we add the half-reactions and eliminate common terms.

Solution



Each balanced half-reaction involves a transfer of two electrons. Because there are the same numbers of electrons on opposite sides in each half-reaction, we can directly add them together and cancel the electrons on each side.



Check for mass balance: All elements appear in equal numbers on both sides.

Check for charge balance: Each side has a total charge of 4−.

► Each I_2 gains $2e^-$. I_2 is reduced; it is the oxidizing agent.

► Each $\text{S}_2\text{O}_3^{2-}$ ion loses an e^- . $\text{S}_2\text{O}_3^{2-}$ is oxidized; it is the reducing agent.

► Oxidizing and reducing agents were defined in Section 6-5.

11-5 Adding H^+ , OH^- , or H_2O to Balance Oxygen or Hydrogen

Frequently we need more oxygen or hydrogen to complete the mass balance for a reaction or half-reaction in aqueous solution. We must be careful, however, not to introduce other changes in oxidation number or to use species that could not actually be present in the solution. We cannot add H_2 or O_2 to equations because these species are not present in aqueous solutions. Acidic solutions do not contain significant concentrations of OH^- ions. Basic solutions do not contain significant concentrations of H^+ ions.

STOP & THINK

If H^+ , H_3O^+ , or any other acid appears on either side of the unbalanced equation, the solution is acidic. If OH^- or any other base appears on either side of the unbalanced equation, the solution is basic.

In acidic solution: We add H^+ or H_2O (*do not add OH^- in acidic solution*).
In basic solution: We add OH^- or H_2O (*do not add H^+ in basic solution*).

The following chart shows how to balance hydrogen and oxygen.

In acidic or neutral solution:

To balance O

For *each* O needed, add *one* H_2O

and ↓ then

To balance H

For *each* H needed, add *one* H^+

In basic solution:

To balance O

For *each* O needed, add *one* H_2O

and ↓ then

To balance H

For *each* H needed, add *one* H_2O to side needing H *and* add *one* OH^- to *other* side
(This adds H without changing O)

► In Section 6-2, we first wrote the *formula unit equation*. We separated any ionized or dissociated species into ions to obtain the *total ionic equation*. Then we eliminated the spectator ions to obtain the *net ionic equation*. In Examples 11-11 and 11-12, we reverse the procedure.

When balancing redox equations, we often find it convenient to omit the spectator ions (see Section 6-2) so that we can focus on the oxidation and reduction processes. We use the methods presented in this chapter to balance the net ionic equation. If necessary we then add the spectator ions and combine species to write the balanced formula unit equation. Examples 11-11 and 11-12 illustrate this approach.

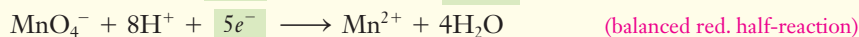
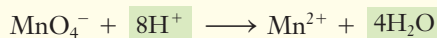
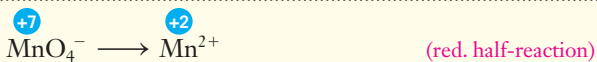
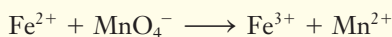
EXAMPLE 11-11 Balancing Net Ionic Equations (Acidic Solution)

Permanganate ions oxidize iron(II) to iron(III) in sulfuric acid solution. Permanganate ions are reduced to manganese(II) ions. Write the balanced net ionic equation for this reaction.

Plan

We use the given information to write as much of the equation as possible. Then we follow Steps 2 through 8 in Section 11-4. The reaction occurs in H_2SO_4 solution; we can add H^+ and H_2O as needed to balance H and O in the half-reactions (Step 3).

Solution



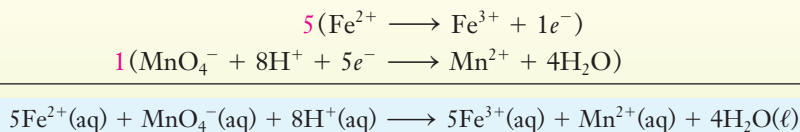
The oxidation half-reaction involves one electron, and the reduction half-reaction involves five electrons. Now we balance the number of electrons transferred in each half-reaction by multiplying each half-reaction by an integer factor. Then we add the two half-reactions and



Potassium permanganate, KMnO_4 , is a commonly used oxidizing agent in the laboratory.

Unless otherwise noted, all content on this page is © Cengage Learning.

cancel out the equal number of electrons on each side. This gives the balanced net ionic equation.



Check for mass balance: All elements appear in equal numbers on both sides.

Check for charge balance: Each side has a total charge of 17+.

STOP & THINK

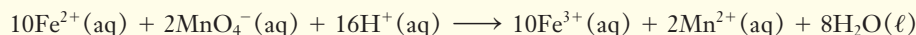
In a balanced net ionic equation, the total charge on the left side of the equation must equal the total charge on the right side.

EXAMPLE 11-12 Net Ionic to Total Ionic and Formula Unit Equations

Write the balanced total ionic and the formula unit equations for the reaction in Example 11-11, given that the reactants were KMnO₄, FeSO₄, and H₂SO₄.

Plan

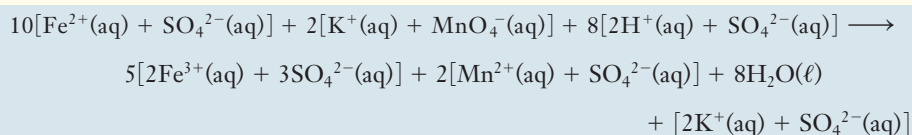
The cationic spectator ion is K⁺, and the anionic spectator ion is SO₄²⁻. The Fe³⁺ ion will need to occur twice in the product Fe₂(SO₄)₃, so there must be an even number of Fe atoms. So the net ionic equation is multiplied by two. It now becomes



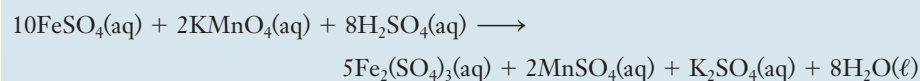
Based on the 10Fe²⁺ and the 16H⁺, we add 18SO₄²⁻ to the reactant side of the equation; we must also add them to the product side to keep the equation balanced. Based on the 2MnO₄⁻, we add 2K⁺ to each side of the equation.

Solution

Total ionic equation



Balanced formula unit equation



Check for mass balance: All elements appear in equal numbers on both sides.

Check for charge balance: There is no net charge on either side of a properly balanced total ionic or formula unit equation.

You should now work Exercise 58.

► The formulas FeSO₄ and H₂SO₄ tell us that there is one SO₄²⁻ for every Fe²⁺, and one SO₄²⁻ for every two H⁺.



Problem-Solving Tip Converting Ionic to Formula Unit Equations

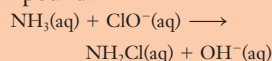
We learned in Section 6-2 how to convert the formula unit equation to the net ionic equation. To do this, we convert the formulas for all *strong electrolytes* into their ions, and then cancel *spectator ions* from both sides of the equation. When balancing redox equations, we often need to reverse this procedure, as illustrated in Example 11-12. To remove the excess charge that remains in a balanced *net ionic* equation, we must add negatively charged spectator ions to combine with positively charged reactants, and we add positively charged spectator ions to combine with negatively charged reactants. Any spectator ions added to the reactant side of the equation must also be added to the product side. Then we combine species to give complete formula units.

STOP & THINK

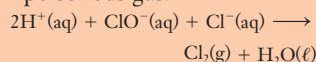
Spectator ions appear in solution on both sides of the total ionic equation, and undergo no change in the chemical reaction. Review Section 6-2 to be sure you understand how to recognize spectator ions.

**CAUTION!**

These common household chemicals, ammonia and bleach, should never be mixed because they react to form chloramine (NH_2Cl), a very poisonous volatile compound.

**CAUTION!**

These common household chemicals, vinegar and bleach, should never be mixed because they react to form chlorine, a very poisonous gas.

**STOP & THINK**

Consider the spectator ions in Exercise 11-13 to be Na^+ , and write the total ionic and formula unit equations for the reaction.

Household bleaches sold under trade names such as Clorox and Purex are 5% solutions of sodium hypochlorite. The hypochlorite ion is a very strong oxidizing agent in basic solution. It oxidizes many stains to colorless substances.

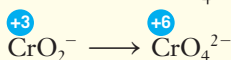
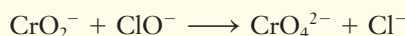
EXAMPLE 11-13 Balancing Redox Equations (Basic Solution)

In basic solution, hypochlorite ions, ClO^- , oxidize chromite ions, CrO_2^- , to chromate ions, CrO_4^{2-} , and are reduced to chloride ions. Write the balanced net ionic equation for this reaction.

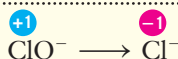
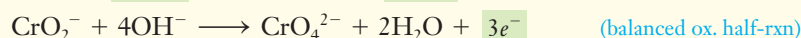
Plan

We are given the formulas for two reactants and two products; we write as much of the equations as possible. The reaction occurs in basic solution; we can add OH^- and H_2O as needed.

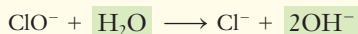
We construct and balance the appropriate half-reactions, equalize the number of electrons in each balanced half-reaction, add the half-reactions, and eliminate common terms. Tracking oxidation states of the key atoms involved in oxidation and reduction can be quite useful as shown below.

Solution

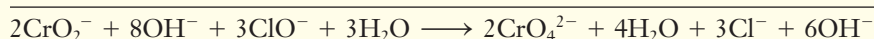
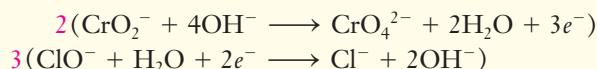
(ox. half-rxn)



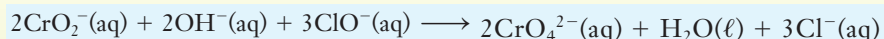
(red. half-rxn)



The oxidation half-reaction involves three electrons, and the reduction half-reaction involves two electrons. We balance the number of electrons transferred in each half-reaction by multiplying each half-reaction by an integer factor. Then we add the two half-reactions together and cancel out the equal number of electrons on each side.



We see that 6OH^- and $3\text{H}_2\text{O}$ can be eliminated from both sides to give the balanced net ionic equation.



Check for mass balance: All elements appear in equal numbers on both sides.

Check for charge balance: Each side has a total charge of 7^- .

You should now work Exercise 54.

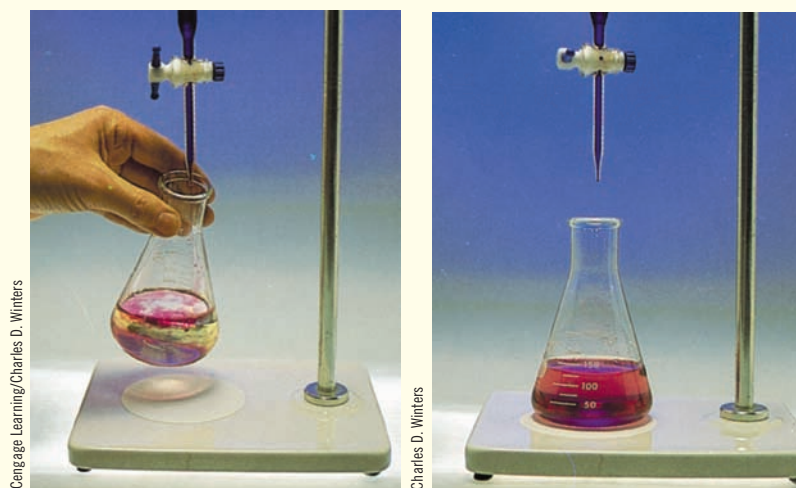
11-6 Calculations for Redox Titrations

One method of analyzing samples quantitatively for the presence of *oxidizable* or *reducible* substances is by **redox titration**. In such analyses, the concentration of a solution is determined by allowing it to react with a carefully measured amount of a *standard* solution of an oxidizing or reducing agent. As in other kinds of chemical reactions, we must pay close attention to the mole ratio in which oxidizing agents and reducing agents react. This is even more important for redox titrations where 1:1 reaction ratios, common for acid–base reactions, are rare.

Potassium permanganate, KMnO_4 , is a strong oxidizing agent. Through the years it has been the “workhorse” of redox titrations. For example, in acidic solution, KMnO_4 reacts with iron(II) sulfate, FeSO_4 , according to the balanced equation in the following example. A strong acid, such as H_2SO_4 , is used in such titrations (see Example 11-11).

EXAMPLE 11-14 Redox Titration

What volume of 0.0250 M KMnO_4 solution is required to oxidize 40.0 mL of 0.100 M FeSO_4 in sulfuric acid solution (Figure 11-2)?



A Nearly colorless FeSO_4 solution is titrated with deep-purple KMnO_4 .

B The end point is the point at which the solution becomes pink, owing to a *very small* excess of KMnO_4 . Here a considerable excess of KMnO_4 was added so that the pink color could be reproduced photographically.

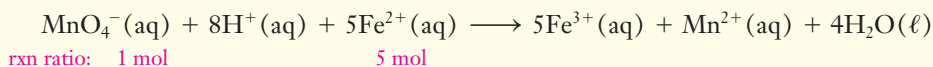
Figure 11-2

Plan

The balanced equation in Example 11-11 gives the reaction ratio, 1 mol MnO_4^- /5 mol Fe^{2+} . Then we calculate the number of moles of Fe^{2+} to be titrated, which lets us find the number of moles of MnO_4^- required, and then the volume in which this number of moles of KMnO_4 is contained.

Solution

The reaction ratio is



The number of moles of Fe^{2+} to be titrated is

$$\underline{\hspace{1cm}} \text{ mol Fe}^{2+} = 40.0 \text{ mL} \times \frac{0.100 \text{ mol Fe}^{2+}}{1000 \text{ mL}} = 4.00 \times 10^{-3} \text{ mol Fe}^{2+}$$

We use the balanced equation to find the number of moles of MnO_4^- required.

$$\underline{\hspace{1cm}} \text{ mol MnO}_4^- = 4.00 \times 10^{-3} \text{ mol Fe}^{2+} \times \frac{1 \text{ mol MnO}_4^-}{5 \text{ mol Fe}^{2+}} = 8.00 \times 10^{-4} \text{ mol MnO}_4^-$$

Each formula unit of KMnO_4 contains one MnO_4^- ion, and so

$$1 \text{ mol KMnO}_4 = 1 \text{ mol MnO}_4^-$$

The volume of 0.0250 M KMnO_4 solution that contains 8.00×10^{-4} mol of KMnO_4 is

$$\begin{aligned} \underline{\hspace{1cm}} \text{ mL KMnO}_4 \text{ soln} &= 8.00 \times 10^{-4} \text{ mol KMnO}_4 \times \frac{1000 \text{ mL KMnO}_4 \text{ soln}}{0.0250 \text{ mol KMnO}_4} \\ &= 32.0 \text{ mL KMnO}_4 \text{ soln} \end{aligned}$$

You should now work Exercises 62 and 64.

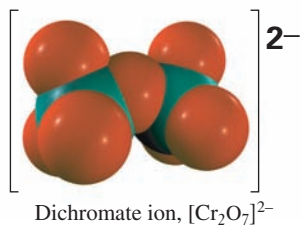
► Because it has an intense purple color, KMnO_4 acts as its own indicator. One drop of 0.020 M KMnO_4 solution imparts a pink color to a liter of pure water. When KMnO_4 solution is added to a solution of a reducing agent, the end point in the titration is taken as the point at which a pale pink color appears in the solution being titrated and persists for at least 30 seconds.

STOP & THINK

One mole of KMnO_4 contains one mole of MnO_4^- ions. The number of moles of KMnO_4 is therefore *always* equal to the number of moles of MnO_4^- ions required in a reaction. Similarly, one mole of FeSO_4 contains 1 mole of Fe^{2+} ions.

STOP & THINK

As before, carefully constructed unit factors, including the reaction ratio, allow us to solve the problem. The concentrations of FeSO_4 and KMnO_4 solutions are similar, so it is reasonable that the volumes of solutions required are similar.



Cengage Learning/Charles Steele

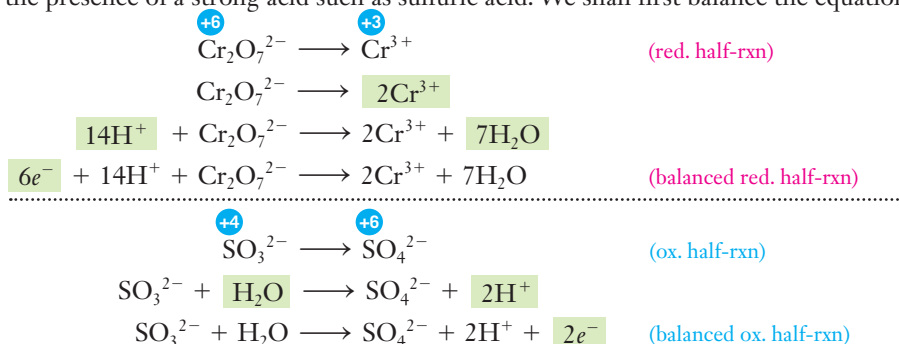


$\text{Cr}_2(\text{SO}_4)_3$ is green in acidic solution.
 $\text{K}_2\text{Cr}_2\text{O}_7$ is orange in acidic solution.

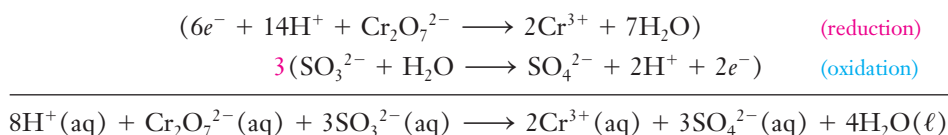
A word about terminology. The reaction involves MnO_4^- ions and Fe^{2+} ions in acidic solution. The source of MnO_4^- ions usually is the soluble ionic compound KMnO_4 . We often refer to “permanganate solutions.” Such solutions also contain cations—in this case, K^+ . Likewise, we often refer to “iron(II) solutions” without specifying what the anion is.

Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, is another frequently used oxidizing agent. However, an indicator must be used when reducing agents are titrated with dichromate solutions. $\text{K}_2\text{Cr}_2\text{O}_7$ is orange, and its reduction product, Cr^{3+} , is green. Neither color is as intense as KMnO_4 , and the transition from orange to green is not as distinct. This is why an intensely colored indicator must be used with $\text{Cr}_2\text{O}_7^{2-}$.

Consider the oxidation of sulfite ions, SO_3^{2-} , to sulfate ions, SO_4^{2-} , by $\text{Cr}_2\text{O}_7^{2-}$ ions in the presence of a strong acid such as sulfuric acid. We shall first balance the equation.



We now equalize the electron transfer, add the balanced half-reactions, and eliminate common terms.



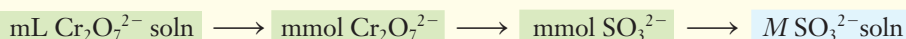
The balanced equation tells us that the reaction ratio is 3 mol SO_3^{2-} /mol $\text{Cr}_2\text{O}_7^{2-}$ or 1 mol $\text{Cr}_2\text{O}_7^{2-}$ /3 mol SO_3^{2-} . Potassium dichromate is the usual source of $\text{Cr}_2\text{O}_7^{2-}$ ions, and Na_2SO_3 is the usual source of SO_3^{2-} ions. Thus, the preceding reaction ratio could also be expressed as 1 mol $\text{K}_2\text{Cr}_2\text{O}_7$ /3 mol Na_2SO_3 .

EXAMPLE 11-15 Redox Titration

A 20.00-mL sample of Na_2SO_3 was titrated with 36.30 mL of 0.05130 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution in the presence of H_2SO_4 . Calculate the molarity of the Na_2SO_3 solution.

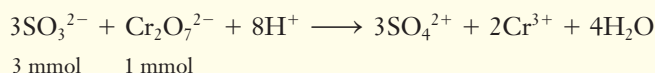
Plan

We can calculate the number of millimoles of $\text{Cr}_2\text{O}_7^{2-}$ in the standard solution. Then we refer to the balanced equation in the preceding discussion, which gives us the reaction ratio, 3 mmol SO_3^{2-} /1 mmol $\text{Cr}_2\text{O}_7^{2-}$. The reaction ratio lets us calculate the number of millimoles of SO_3^{2-} (Na_2SO_3) that reacted and the molarity of the solution.



Solution

From the preceding discussion we know the balanced equation and the reaction ratio.



The number of millimoles of $\text{Cr}_2\text{O}_7^{2-}$ used is

$$\underline{\hspace{1cm}} \text{ mmol Cr}_2\text{O}_7^{2-} = 36.30 \text{ mL} \times \frac{0.05130 \text{ mmol Cr}_2\text{O}_7^{2-}}{\text{mL}} = 1.862 \text{ mmol Cr}_2\text{O}_7^{2-}$$

The number of millimoles of SO_3^{2-} that reacts with 1.862 mmol of $\text{Cr}_2\text{O}_7^{2-}$ is

$$\underline{\quad} \text{ mmol } \text{SO}_3^{2-} = 1.862 \text{ mmol } \text{Cr}_2\text{O}_7^{2-} \times \frac{3 \text{ mmol } \text{SO}_3^{2-}}{1 \text{ mmol } \text{Cr}_2\text{O}_7^{2-}} = 5.586 \text{ mmol } \text{SO}_3^{2-}$$

The Na_2SO_3 solution contains 5.586 mmol of SO_3^{2-} (or 5.586 mmol of Na_2SO_3). Its molarity is

$$\underline{\quad} \frac{\text{mmol } \text{Na}_2\text{SO}_3}{\text{mL}} = \frac{5.586 \text{ mmol } \text{Na}_2\text{SO}_3}{20.00 \text{ mL}} = 0.2793 \text{ M } \text{Na}_2\text{SO}_3$$

You should now work Exercise 66.

STOP & THINK

The volumes of the Na_2SO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ solutions are similar, so it is reasonable that their concentrations are similar. Once again, it is convenient to express molarity as mmol solute/mL solution.

KEY TERMS

Acid–base titration The quantitative analysis of the amount or concentration of an acid or base in a sample by observing its reaction with a known amount or concentration of a base or acid.

Buret A piece of volumetric glassware, usually graduated in 0.1-mL intervals, that is used in titrations to deliver solutions in a quantitative (dropwise) manner.

End point The point at which an indicator changes color and a titration is stopped.

Equivalence point The point at which chemically equivalent amounts of reactants have reacted.

Half-reaction Either the oxidation part or the reduction part of a redox reaction.

Indicator For acid–base titrations, an organic compound that exhibits its different colors in solutions of different acidities; a properly selected indicator is used to determine the point at which the reaction between two solutes is complete.

Millimole 1/1000 mole.

Molarity (M) The number of moles of solute per liter of solution or the number of millimoles of solute per milliliter of solution.

Oxidation An algebraic increase in oxidation number; usually corresponds to a loss of electrons.

Oxidation–reduction reaction A reaction in which oxidation and reduction occur; also known as a *redox reaction*.

Oxidizing agent The substance that oxidizes another substance and is reduced.

Primary standard A substance of a known high degree of purity that undergoes one invariable reaction with the other reactant of interest.

Redox reaction An oxidation–reduction reaction.

Redox titration The quantitative analysis of the amount or concentration of an oxidizing or reducing agent in a sample by observing its reaction with a known amount or concentration of a reducing or oxidizing agent.

Reducing agent The substance that reduces another substance and is oxidized.

Reduction An algebraic decrease in oxidation number; usually corresponds to a gain of electrons.

Secondary standard A solution that has been titrated against a primary standard. A standard solution is a secondary standard.

Standard solution A solution for which the concentration is accurately known.

Standardization The process by which the concentration of a solution is accurately determined by titrating it against an accurately known amount of a primary standard.

Titration A procedure in which a solution of one reactant, the titrant, is carefully added to a solution of another reactant, and the volume of titrant required for complete reaction is measured. The concentration of one solution, usually (but not necessarily) the titrant, is known; this allows one to calculate the concentration or the amount of reactant in the other.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Molarity

- Why can we describe molarity as a “method of convenience” for expressing concentrations of solutions?
- Why is the molarity of a solution the same number whether we describe it in mol/L or in mmol/mL?

- Calculate the molarities of solutions that contain the following masses of solute in the indicated volumes: (a) 35.5 g of H_3AsO_4 in 500. mL of solution; (b) 8.33 g of $(\text{COOH})_2$ in 600. mL of solution; (c) 8.25 g of $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ in 750. mL of solution.

● **Molecular Reasoning** exercises

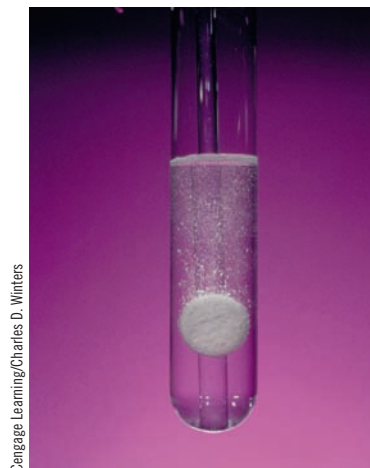
▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

4. What is the molarity of a solution made by dissolving 41.4 g of magnesium sulfate in sufficient water to produce a total of 3.00 L of solution?
5. There are 85.0 g of iron(II) nitrate present in 850. mL of a solution. Calculate the molarity of that solution.
6. Calculate the molarity of a solution that is 39.77% H_2SO_4 by mass. The specific gravity of the solution is 1.305.
7. Calculate the molarity of a solution that is 19.0% HNO_3 by mass. The specific gravity of the solution is 1.11.
8. If 225 mL of 3.35 M HCl solution is added to 426 mL of 1.77 M NaOH solution, the resulting solution will be _____ molar in NaCl. Assume that the volumes are additive.
9. What is the molarity of the salt solution produced when 750. mL of 3.00 M HCl and 750. mL of 3.00 M LiOH are mixed? Assume that the volumes are additive. Give the name and formula of the salt formed.
10. Potassium iodide is sometimes used as a sodium chloride replacement for those people who cannot tolerate table salt. Calculate the molarity of potassium iodide solution produced when 55.5 mL of 8.99 M HI and 35.4 mL of 14.1 M KOH are mixed. Assume that the volumes are additive.
11. If you dilute 25.0 mL of 1.50 M hydrochloric acid to 500. mL, what is the molar concentration of the dilute acid?
12. What is the concentration of barium iodide produced by mixing 7.50 mL of 0.135 M $\text{Ba}(\text{OH})_2$ with 19.4 mL of 0.104 M HI?
13. What is the concentration of the ammonium chloride produced when 21.0 mL of 12.0 M HCl and 17.5 mL of 8.00 M NH_3 are mixed? Assume that the volumes are additive.
14. If 250. mL of 5.52 M H_3PO_4 solution is added to 775 mL of 5.52 M NaOH solution, the resulting solution will be _____ molar in Na_3PO_4 and _____ molar in _____.
15. If 100. mL of 0.200 M HCl solution is added to 200. mL of 0.0400 M $\text{Ba}(\text{OH})_2$ solution, the resulting solution will be _____ molar in BaCl_2 and _____ molar in _____.
16. A vinegar solution is 5.11% acetic acid. Its density is 1.007 g/mL. What is its molarity?
17. A household ammonia solution is 5.03% ammonia. Its density is 0.979 g/mL. What is its molarity?
18. (a) What volumes of 3.25 M NaOH and 4.50 M H_3PO_4 solutions would be required to form 1.00 mol of Na_3PO_4 ? (b) What volumes of the solutions would be required to form 1.00 mol of Na_2HPO_4 ?
21. Distinguish between the *net ionic equation* and the *formula unit equation*.
22. (a) What is potassium hydrogen phthalate, KHP? (b) What is its major use?
23. Why can sodium carbonate be used as a primary standard for solutions of acids?
24. What volume of 0.145 M acetic acid solution would completely neutralize 21.58 mL of 0.105 M $\text{Ba}(\text{OH})_2$ solution?
25. What volume of 0.150 M potassium hydroxide solution would completely neutralize 29.1 mL of 0.100 M H_2SO_4 solution?
26. Calculate the molarity of a solution of HNO_3 if 19.55 mL of the solution neutralizes 0.2040 g of Na_2CO_3 .
27. If 35.38 mL of a sulfuric acid solution reacts completely with 0.3545 g of Na_2CO_3 , what is the molarity of the sulfuric acid solution?
28. A solution of sodium hydroxide is standardized against potassium hydrogen phthalate. From the following data, calculate the molarity of the NaOH solution.

mass of KHP	0.5536 g
buret reading before titration	0.23 mL
buret reading after titration	37.26 mL
29. Calculate the molarity of a KOH solution if 30.68 mL of the KOH solution reacted with 0.4178 g of potassium hydrogen phthalate, KHP.



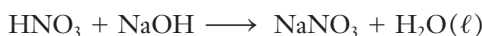
Cengage Learning/Charles D. Winters

Antacid tablet reacting with HCl solution

Standardization and Acid–Base Titrations

19. Define and illustrate the following terms clearly and concisely: (a) standard solution; (b) titration; (c) primary standard; (d) secondary standard.
20. Describe the preparation of a standard solution of NaOH, a compound that absorbs both CO_2 and H_2O from the air.
30. Calcium carbonate tablets can be used as an antacid and a source of dietary calcium. A bottle of generic antacid tablets states that each tablet contains 900. mg calcium carbonate. What volume of 1.0 M HCl could be neutralized by the calcium carbonate in one tablet?
31. What volume of 9.00 M H_2SO_4 is required to react with 65.5 mL of 6.00 M NaOH to produce a Na_2SO_4 solution? What volume of water must be added to the resulting solution to obtain a 1.25 M Na_2SO_4 solution?
32. (a) What are the properties of an ideal primary standard? (b) What is the importance of each property?

33. ● The secondary standard solution of NaOH of Exercise 28 was used to titrate a solution of unknown concentration of HCl. A 30.00-mL sample of the HCl solution required 28.21 mL of the NaOH solution for complete neutralization. What is the molarity of the HCl solution?
34. ▲ An impure sample of $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ that had a mass of 1.00 g was dissolved in water and titrated with standard NaOH solution. The titration required 19.16 mL of 0.298 M NaOH solution. Calculate the percent $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ in the sample. Assume that the sample contains no acidic impurities.
35. ▲ A 25.0-mL sample of 0.0500 M $\text{Ca}(\text{OH})_2$ is added to 10.0 mL of 0.100 M HNO_3 . (a) Is the resulting solution acidic or basic? (b) How many moles of excess acid or base are present? (c) How many additional mL of 0.0500 M $\text{Ca}(\text{OH})_2$ or 0.100 M HNO_3 would be required to completely neutralize the solution?
36. ▲ An antacid tablet containing calcium carbonate as an active ingredient required 26.8 mL of 0.112 M HCl for complete neutralization. What mass of CaCO_3 did the tablet contain?
37. ● ▲ Butyric acid, whose empirical formula is $\text{C}_2\text{H}_4\text{O}$, is the acid responsible for the odor of rancid butter. The acid has one ionizable hydrogen per molecule. A 1.000-g sample of butyric acid is neutralized by 36.28 mL of 0.3132 M NaOH solution. What are (a) the molecular weight and (b) the molecular formula of butyric acid?
38. What is the molarity of a solution of sodium hydroxide, NaOH, if 41.4 mL of this solution is required to react with 37.5 mL of 0.0342 M nitric acid solution according to the following reaction?



39. What is the molarity of a solution of sodium hydroxide, NaOH, if 18.45 mL of this solution is required to react with 17.60 mL of 0.101 M hydrochloric acid solution according to the following reaction?
- $$\text{HCl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{H}_2\text{O}(\ell)$$
40. What is the molarity of a solution that contains 0.978 g of H_3PO_4 in 185 mL of solution? How many milliliters of this solution could be completely neutralized by 11.58 mL of 0.454 M NaOH?
41. What is the molarity of a sulfuric acid solution that is 19.6% H_2SO_4 by mass? The density of the solution is 1.14 g/mL. How many milliliters of this solution could be completely neutralized by 11.58 mL of 0.454 M NaOH?
42. Calculate the molarity of a solution that contains 8.6 g of arsenic acid, H_3AsO_4 , in enough water to make 475 mL of solution. How many milliliters of this solution could be completely neutralized by 11.58 mL of 0.454 M NaOH?
43. What volume, in milliliters, of 0.512 M NaOH is required to react completely with 25.0 mL 0.234 M H_2SO_4 ?
44. Calculate the molarity of an HCl solution if 39.1 mL of the solution reacts with 0.483 g of Na_2CO_3 .



45. ● To minimize the effect of buret reading errors, titrations performed using a 50-mL buret are most accurate when titrant volumes are in the range of 35 to 45 mL. Suggest a range of sample weights that would yield a 35- to 45-mL titration range for the standardization of solutions of the following approximate concentrations. (a) 0.0533 M NaOH using potassium hydrogen phthalate (KHP), a monoprotic acid. (b) 0.0895 M KOH using primary standard benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$), a monoprotic acid.
46. ▲ Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, is commonly used as the active ingredient in antacid tablets. A student analyzed an antacid tablet for mass percent $\text{Mg}(\text{OH})_2$ by dissolving a tablet weighing 1.462 g in 25.00 mL of 0.953 M HCl, and neutralizing the unreacted HCl. That neutralization required 12.29 mL of 0.602 M NaOH. Calculate the mass percent of $\text{Mg}(\text{OH})_2$ in the antacid tablet.
47. Vinegar is an aqueous solution of acetic acid, CH_3COOH . Suppose you titrate a 25.00-mL sample of vinegar with 17.62 mL of a standardized 0.1045 N solution of NaOH. (a) What is the molarity of acetic acid in this vinegar? (b) What is the mass of acetic acid contained in 1.000 L of vinegar?

Balancing Redox Equations

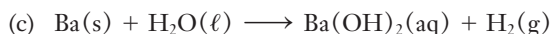
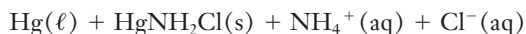
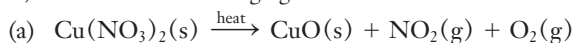
In Exercises 48 and 49, write balanced formula unit equations for the reactions described by words.

48. ▲ (a) Iron reacts with hydrochloric acid to form aqueous iron(II) chloride and gaseous hydrogen. (b) Chromium reacts with sulfuric acid to form aqueous chromium(III) sulfate and gaseous hydrogen. (c) Tin reacts with concentrated nitric acid to form tin(IV) oxide, nitrogen dioxide, and water.
49. (a) Carbon reacts with hot concentrated nitric acid to form carbon dioxide, nitrogen dioxide, and water. (b) Sodium reacts with water to form aqueous sodium hydroxide and gaseous hydrogen. (c) Zinc reacts with sodium hydroxide solution to form aqueous sodium tetrahydroxozincate and gaseous hydrogen. (The tetrahydroxozincate ion is $[\text{Zn}(\text{OH})_4]^{2-}$.)
50. ● Copper is a widely used metal. Before it is welded (brazed), copper is cleaned by dipping it into nitric acid. HNO_3 oxidizes Cu to Cu^{2+} ions and is reduced to NO. The other product is H_2O . Write the balanced net ionic and formula unit equations for the reaction. Excess HNO_3 is present.

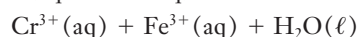
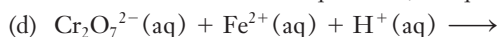
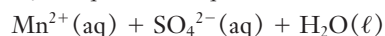
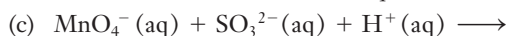
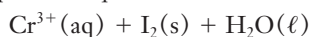
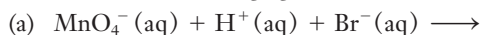


Copper is cleaned by dipping it into nitric acid

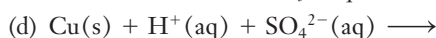
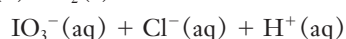
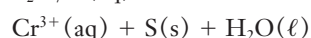
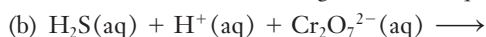
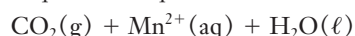
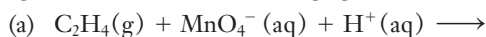
51. Balance the following equations. For each equation tell what is oxidized, what is reduced, what the oxidizing agent is, and what the reducing agent is.



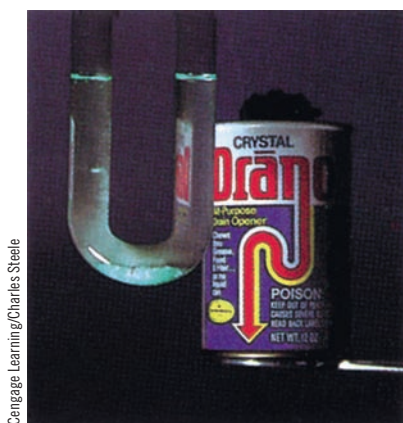
52. Balance the following equations. For each equation tell what is oxidized, what is reduced, what the oxidizing agent is, and what the reducing agent is.



53. Balance the following ionic equations. For each equation tell what is oxidized, what is reduced, what the oxidizing agent is, and what the reducing agent is.

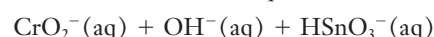
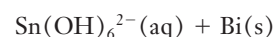
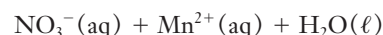
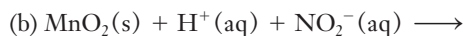
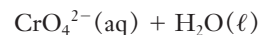


54.  Drano drain cleaner is solid sodium hydroxide that contains some aluminum chips. When Drano is added to water, the NaOH dissolves rapidly with the evolution of a lot of heat. The Al reduces H_2O in the basic solution to produce $[\text{Al}(\text{OH})_4]^-$ ions and H_2 gas, which gives the bubbling action. Write the balanced net ionic and formula unit equations for this reaction.

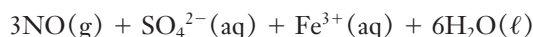
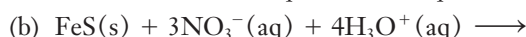
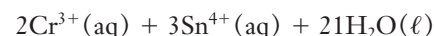
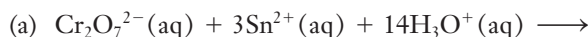


The Drano reaction

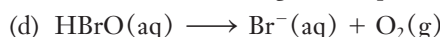
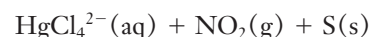
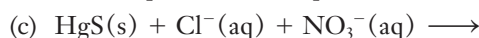
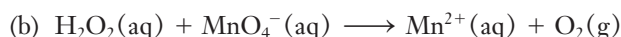
55. Balance the following ionic equations. For each equation tell what is oxidized, what is reduced, what the oxidizing agent is, and what the reducing agent is.



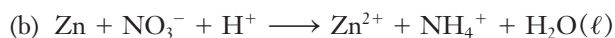
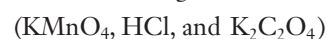
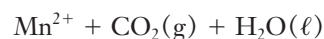
56. In the following reactions, decide which reactant is oxidized and which is reduced. Designate the oxidizing agent and the reducing agent.



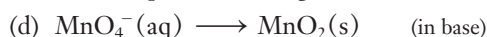
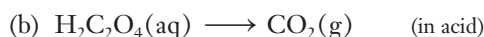
57. Balance the following ionic equations for reactions in acidic solution. H^+ or H_2O (but not OH^-) may be added as necessary.



58. Write the balanced net ionic equations for the reactions given. Then, using the reactants shown in parentheses, convert each balanced net ionic equation to a balanced formula unit equation.

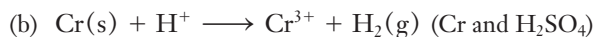
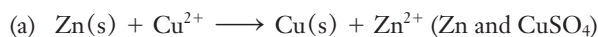


59. Write balanced equations for the following half-reactions. Specify whether each is an oxidation or reduction.

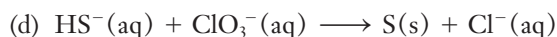
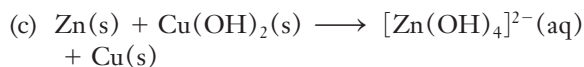
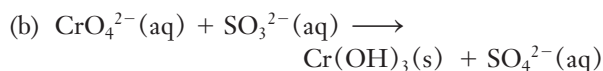
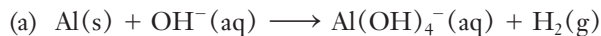


60. Write the balanced net ionic equations for the reactions given. Then, using the reactants shown in parentheses,

convert each balanced net ionic equation to a balanced formula unit equation.



61. Balance the following redox equations. All occur in basic solution.



Redox Titrations

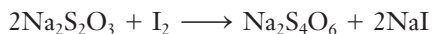
62. ▲ What volume of 0.233 *M* KMnO_4 would be required to oxidize 25.0 mL of 0.150 *M* FeSO_4 in acidic solution?

63. What volume of 0.142 *M* $\text{K}_2\text{Cr}_2\text{O}_7$ would be required to oxidize 70.0 mL of 0.100 *M* Na_2SO_3 in acidic solution? The products include Cr^{3+} and SO_4^{2-} ions.

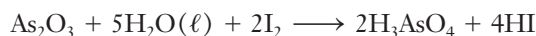
64. What volume of 0.190 *M* KMnO_4 would be required to oxidize 27.0 mL of 0.150 *M* KI in acidic solution? Products include Mn^{2+} and I_2 .

65. What volume of 0.190 *M* $\text{K}_2\text{Cr}_2\text{O}_7$ would be required to oxidize 27.0 mL of 0.250 *M* KI in acidic solution? Products include Cr^{3+} and I_2 .

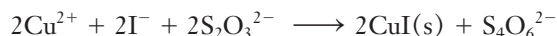
66. (a) A solution of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, is 0.1442 *M*. 37.00 mL of this solution reacts with 28.85 mL of I_2 solution. Calculate the molarity of the I_2 solution.



(b) 35.32 mL of the I_2 solution is required to titrate a sample containing As_2O_3 . Calculate the mass of As_2O_3 (197.8 g/mol) in the sample.



67. Copper(II) ions, Cu^{2+} , can be determined by the net reaction

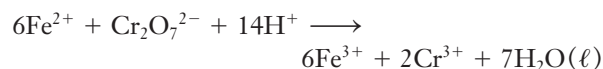


A 4.115-g sample containing CuSO_4 and excess KI is titrated with 32.55 mL of 0.2214 *M* solution of $\text{Na}_2\text{S}_2\text{O}_3$. What is the percent CuSO_4 (159.6 g/mol) in the sample?

68. What volume of 5.0 *M* nitrate ion solution would be required to react with 35. mL of 0.75 *M* sulfide ion solution? (Hint: The equation is not balanced.)



69. ▲ The iron in a 6.675-g sample containing some Fe_2O_3 is reduced to Fe^{2+} . The Fe^{2+} is titrated with 14.42 mL of 0.1467 *M* $\text{K}_2\text{Cr}_2\text{O}_7$ in an acid solution.



Find (a) the mass of Fe and (b) the percentage of Fe in the sample.

70. Calculate the molarity of a solution that contains 14.6 g of KMnO_4 in 750. mL of solution to be used in the reaction that produces MnO_4^{2-} ions as the reduction product.
71. ▲ A 0.855-g sample of an ore of iron is dissolved in acid and converted to Fe(II) . The sample is oxidized by 36.50 mL of 0.161 *M* ceric sulfate, $\text{Ce(SO}_4)_2$, solution; the cerium(IV) ion, Ce^{4+} , is reduced to Ce^{3+} ion. (a) Write a balanced equation for the reaction. (b) What is the percent iron in the ore?

Mixed Exercises

72. Calculate the molarity of the solute in a solution containing

- (a) 0.0618 g MgNH_4PO_4 in 250. mL solution
 (b) 16.8 g NaCH_3COO in 300. mL solution
 (c) 0.0250 g CaC_2O_4 in 750. mL solution
 (d) 2.20 g $(\text{NH}_4)_2\text{SO}_4$ in 400. mL solution

73. Calculate the molarity of a sulfuric acid solution if 38.75 mL of it reacts completely with 0.3911 g of sodium carbonate.

74. Find the number of mmol of HCl that reacts with 25.5 mL of 0.298 *M* NaOH . What volume of 0.606 *M* HCl is needed to furnish this amount of HCl ?

75. What is the composition of the final solution when 25.5 mL of 0.298 *M* NaOH and 24.5 mL of 0.410 *M* HCl solutions are mixed?

76. What volume of 0.1153 *M* HCl is needed to completely neutralize 1.98 g of Ca(OH)_2 ?

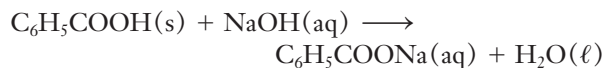
77. What mass of NaOH is needed to neutralize 34.50 mL of 0.1036 *M* HCl ? If the NaOH is available as a 0.1533 *M* aqueous solution, what volume will be required?

78. What volume of 0.296 *M* H_2SO_4 solution would be required to neutralize completely 34.4 mL of 0.296 *M* KOH solution?

79. What volume of 0.344 *M* H_2SO_4 solution would be required to neutralize completely 34.4 mL of 0.255 *M* KOH solution?

80. What volume of 0.1945 *M* sodium hydroxide would be required to neutralize completely 29.41 mL of 0.1023 *M* H_2SO_4 solution?

81. Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, is sometimes used as a primary standard for the standardization of solutions of bases. A 1.862-g sample of this acid is neutralized by 35.00 mL of NaOH solution. What is the molarity of the base solution?



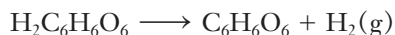
82. Find the volume of 0.245 *M* HI solution required to titrate

- (a) 25.0 mL of 0.100 *M* NaOH
 (b) 0.503 g of AgNO_3 ($\text{Ag}^+ + \text{I}^- \longrightarrow \text{AgI(s)}$)
 (c) 0.621 g CuSO_4 ($2\text{Cu}^{2+} + 4\text{I}^- \longrightarrow 2\text{CuI(s)} + \text{I}_2(\text{s})$)

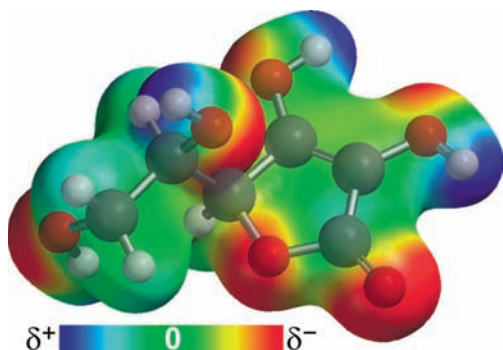


Conceptual Exercises

83. Describe how you could prepare 1.00 L of $1.00 \times 10^{-6} M$ NaCl solution by using a balance that can measure masses only to the nearest 0.01 g.
84. ● Ascorbic acid (vitamin C), along with having many other reputed properties, acts as an antioxidant. The following equation illustrates its antioxidant properties.



What is an antioxidant? Assign oxidation numbers. Is vitamin C oxidized or reduced in this reaction?



85. ● For each of the following substances, give at least one reason why it would be unacceptable as a primary standard for standardizing aqueous solutions of bases: benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, technical grade (99.0% purity); calcium chloride, CaCl_2 , which is hygroscopic; chenodeoxycholic acid, $\text{C}_{24}\text{H}_{40}\text{O}_4$, a monoprotic acid synthesized in the liver from cholesterol; chromic acid, H_2CrO_4 ; hydrocyanic acid, HCN ; hydrofluoric acid, HF ; stearic acid, $\text{C}_{17}\text{H}_{35}\text{COOH}$, which is insoluble in water; sulfuric acid, H_2SO_4 .

86. ● When 100. mL of 0.100 M HCl solution and 100. mL of 0.100 M NaOH are mixed,

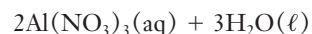
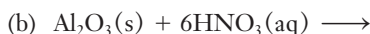
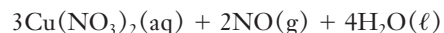


0.0100 mole of HCl reacts completely with 0.0100 mole of NaOH, producing 0.0100 mole of NaCl. Assuming that the amount of water produced by the reaction is negligible, the molarity of the salt in the resulting solution is 0.0500 M NaCl. Is the amount of water produced really negligible? Calculate the volume of water produced by the reaction. Add this volume to the final volume (200. mL).

Is the amount of water produced significant? If the initial volumes had been given as 100.0 mL of 0.1000 M HCl solution and 100.0 mL of 0.1000 M NaOH, would the addition of the volume of water produced by the reaction have been significant?

Building Your Knowledge

87. For the formation of 1.00 mol of water, which reaction uses the most nitric acid?



88. ● Limonite is an ore of iron that contains $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. A 0.5166-g sample of limonite is dissolved in acid and treated so that all the iron is converted to ferrous ions, Fe^{2+} . This sample requires 42.96 mL of 0.02130 M sodium dichromate solution, $\text{Na}_2\text{Cr}_2\text{O}_7$, for titration. Fe^{2+} is oxidized to Fe^{3+} , and $\text{Cr}_2\text{O}_7^{2-}$ is reduced to Cr^{3+} . What is the percent iron in the limonite? If your answer had been over 100% limonite, what conclusion could you make, presuming that the analytical data are correct?

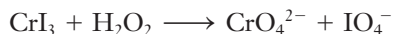
89. One of the troublesome products of a water treatment plant in some areas of the country is $\text{Mg}(\text{OH})_2$, a gelatinous precipitate formed during water softening. A suggestion was made that instead of shoveling the precipitate out of the pool during cleaning, the $\text{Mg}(\text{OH})_2$ could be neutralized with hydrochloric acid to produce a soluble compound, MgCl_2 . Then the pool could be flushed out with fresh water. Calculate the volume of 12.0 M HCl necessary to neutralize 3750 L of solution containing 1.50 g of $\text{Mg}(\text{OH})_2$ per liter.

90. Silver nitrate and calcium chloride solutions produce a heavy, white precipitate when mixed. Chemical analysis indicates that the precipitate is silver chloride. What mass of silver chloride would be produced if 95 mL of 6.0 M silver nitrate is mixed with 40 mL of 6.0 M calcium chloride?

91. A 0.500-g sample of a crystalline monoprotic acid was dissolved in sufficient water to produce 100. mL of solution. Neutralization of the resulting solution required 75.0 mL of 0.150 M NaOH. How many moles of the acid were present in the initial acid solution?

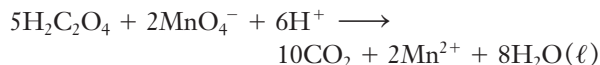
92. The typical concentration of hydrochloric acid in stomach acid (digestive juice) is about $8.0 \times 10^{-2} M$. One experiences "acid stomach" when the stomach contents reach about $1.0 \times 10^{-1} M$ HCl. One antacid tablet contains 334 mg of active ingredient, $\text{NaAl}(\text{OH})_2\text{CO}_3$. Assume that you have acid stomach and that your stomach contains 800. mL of $1.0 \times 10^{-1} M$ HCl. Calculate the number of mmol of HCl in the stomach and the number of mmol of HCl that the tablet can neutralize. Which is greater? (The neutralization reaction produces NaCl, AlCl_3 , CO_2 , and H_2O .)

93. An unknown crystalline monoprotic acid was analyzed by titration with a 0.295 M NaOH solution. 1.880 g of the acid required 27.82 mL of the base to be neutralized. What is the molecular weight of the acid?
94. ▲ A few redox reactions have more than one oxidation half-reaction or more than one reduction half-reaction. Balancing the equations for these reactions is more complicated. However, the multiple half-reactions are often stoichiometrically linked. Maintain the correct ratio of the elements and balance the electron transfer by multiplying them both by the same integer. Balance the following net ionic equation for a reaction in basic solution. OH^- or H_2O (but not H^+) may be added as necessary.



What is oxidized, what is reduced, what is the oxidizing agent, and what is the reducing agent?

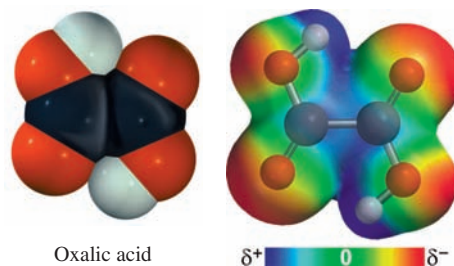
95. ● Write a Lewis formula for the anion SiF_6^{2-} that would be produced from the weak acid H_2SiF_6 . Use the VSEPR theory to predict the shape of SiF_6^{2-} .
96. ● The etching of glass by hydrofluoric acid may be represented by the simplified reaction of silica with HF.
- $$\text{SiO}_2(\text{s}) + \text{HF}(\text{aq}) \longrightarrow \text{H}_2\text{SiF}_6(\text{aq}) + \text{H}_2\text{O}(\ell)$$
- This is an acid–base reaction in which a weak acid is used to produce an even weaker acid. Is it also an oxidation–reduction reaction? Balance the equation.
97. Oxalic acid, a poisonous compound, is found in certain vegetables such as spinach and rhubarb, but in concentrations well below toxic limits. The manufacturers of a spinach juice concentration routinely test their product using an oxalic acid analysis to avoid any problems from an unexpectedly high concentration of this chemical. A titration with potassium permanganate is used for the oxalic acid assay, according to the following net equation.



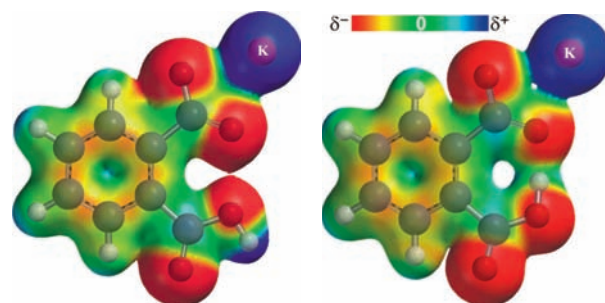
Calculate the molarity of an oxalic acid solution requiring 23.2 mL of 0.127 M permanganate for a 25.0 mL portion of the solution.



Spinach and rhubarb



98. ● ▲ Consider the two electrostatic charge potential plots for potassium hydrogen phthalate (KHP) shown below. Which is more stable (has a lower energy) and why?



Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

99. Use an internet search engine (such as <http://www.google.com>) to locate information on cola soda drinks. (a) What are the acids present in a typical cola? (b) What is the approximate molarity of the principal acid used in a cola?
100. Use an internet search engine (such as <http://www.google.com>) to locate information on each of the following terms. Define three of the four following terms as they relate to titrations: (a) aliquot; (b) analyte; (c) titrant; and (d) scout titration (not associated with Boy Scouts).
101. Use an internet search engine (such as <http://www.google.com>) to locate information on each of the following concepts. Define three of the following four as they relate to titrations: (a) back titration; (b) concave meniscus; (c) Karl Fischer titration; and (d) parallax error.
102. Use an internet search engine (such as <http://www.google.com>) to locate information on “pool chemistry.” Define total alkalinity. Why should a pool owner be concerned about total alkalinity?



Gases and the Kinetic–Molecular Theory

12



The lower density of the hot air trapped in these balloons causes them to rise into the more dense atmosphere.

Jim Lozouski/Shutterstock.com

OUTLINE

- 12-1** Comparison of Solids, Liquids, and Gases
- 12-2** Composition of the Atmosphere and Some Common Properties of Gases
- 12-3** Pressure
- 12-4** Boyle's Law: The Volume–Pressure Relationship
- 12-5** Charles's Law: The Volume–Temperature Relationship; The Absolute Temperature Scale
- 12-6** Standard Temperature and Pressure
- 12-7** The Combined Gas Law Equation
- 12-8** Avogadro's Law and the Standard Molar Volume
- 12-9** Summary of Gas Laws: The Ideal Gas Equation
- 12-10** Determination of Molecular Weights and Molecular Formulas of Gaseous Substances
- 12-11** Dalton's Law of Partial Pressures
- 12-12** Mass–Volume Relationships in Reactions Involving Gases
- 12-13** The Kinetic–Molecular Theory
- 12-14** Diffusion and Effusion of Gases
- 12-15** Deviations from Ideal Gas Behavior

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Understand the properties of gases and compare gases, liquids, and solids
- ▶ Describe how pressure is measured
- ▶ Understand and use the absolute (Kelvin) temperature scale
- ▶ Describe the relationships among pressure, volume, temperature, and amount of gas (Boyle's Law, Charles's Law, Avogadro's Law, and the Combined Gas Law), and the limitations of each
- ▶ Use Boyle's Law, Charles's Law, Avogadro's Law, and the Combined Gas Law, as appropriate, to calculate changes in pressure, volume, temperature, and amount of gas
- ▶ Calculate gas densities and the standard molar volume
- ▶ Use the ideal gas equation to do pressure, volume, temperature, and mole calculations related to gas samples
- ▶ Determine molecular weights and formulas of gaseous substances from measured properties of gases
- ▶ Describe how mixtures of gases behave and predict their properties (Dalton's Law of Partial Pressures)
- ▶ Carry out calculations about the gases involved in chemical reactions
- ▶ Apply the kinetic-molecular theory of gases and describe how this theory is consistent with the observed gas laws
- ▶ Describe molecular motion, diffusion, and effusion of gases
- ▶ Describe the molecular features that are responsible for nonideal behavior of gases; explain when this nonideality is significant

12-1 Comparison of Solids, Liquids, and Gases

Matter exists on earth in three physical states: solids, liquids, and gases. In the solid state H_2O is known as ice, in the liquid state it is called water, and in the gaseous state it is known as steam or water vapor. Most, but not all, substances can exist in all three states. Most solids change to liquids and most liquids turn into gases as they are heated. Liquids and gases are known as **fluids** because they flow freely. Solids and liquids are referred to as **condensed states** because they have much higher densities than gases. Table 12-1 displays the densities of a few common substances in different physical states.

As the data in Table 12-1 indicate, solids and liquids are many times denser than gases. The molecules must be very far apart in gases and much closer together in liquids and solids. For example, the volume of one mole of liquid water is about 18 milliliters, whereas one mole of steam occupies about 30,600 milliliters at 100°C and atmospheric pressure. Gases are easily compressed, and they completely fill any container in which they are present. This tells us that the molecules in a gas are far apart relative to their sizes and that interactions among them are weak. Because they are so far apart, gaseous molecules would not interact with one another were it not for their rapid motion and frequent collisions.

All gases can be liquefied by cooling and compressing them. Volatile liquids easily evaporate to form gases at room temperature or slightly above. The term **vapor** refers to a gas that is formed by evaporation of a liquid or sublimation of a solid. We often use this term when some of the liquid or solid remains in contact with the gas.

▶ *Volatile* liquids evaporate readily. They have low boiling points, typically between room temperature and about 80°C .

Table 12-1 Densities and Molar Volumes of Three Substances at Atmospheric Pressure*

Substance	Solid		Liquid (20°C)		Gas (100°C)	
	Density (g/mL)	Molar Volume (mL/mol)	Density (g/mL)	Molar Volume (mL/mol)	Density (g/mL)	Molar Volume (mL/mol)
Water (H_2O)	0.917 (0°C)	19.6	0.998	18.0	0.000588	30,600
Benzene (C_6H_6)	0.899 (0°C)	86.9	0.876	89.2	0.00255	30,600
Carbon tetrachloride (CCl_4)	1.70 (-25°C)	90.5	1.59	96.8	0.00503	30,600

*The molar volume of a substance is the volume occupied by one mole of that substance.

Unless otherwise noted, all content on this page is © Cengage Learning.

12-2 Composition of the Atmosphere and Some Common Properties of Gases

Many important chemical substances are gases at ambient conditions. The earth's atmosphere is a mixture of gases and particles of liquids and solids (Table 12-2). The major gaseous components are N_2 (bp = -195.79°C) and O_2 (bp = -182.98°C), with smaller concentrations of other gases. All gases are *miscible*; that is, they mix completely *unless* they react with one another.

Several scientists, notably Torricelli (1643), Boyle (1660), Charles (1787), and Graham (1831), laid an experimental foundation on which our present understanding of gases is based. Their investigations showed that

1. Gases can be easily compressed into smaller volumes; that is, their densities can be increased by applying increased pressure.
2. Gases exert pressure on their surroundings; in turn, pressure must be exerted to confine gases.
3. Gases expand without limits, so gas samples completely and uniformly occupy the volume of any container.
4. Gases diffuse into one another, so samples of gas placed in the same container mix completely. Conversely, different gases in a mixture do not separate on standing.
5. The amounts and properties of gases are described in terms of temperature, pressure, the volume occupied, and the number of molecules present. For example, a sample of gas occupies a greater volume when hot than it does when cold at the same pressure, but the number of molecules does not change.

Table 12-2 Composition of Dry Air

Gas	% by Volume
N_2	78.09
O_2	20.94
Ar	0.93
CO_2	0.03*
He, Ne, Kr, Xe	0.002
CH_4	0.00015*
H_2	0.00005
All others combined†	<0.00004

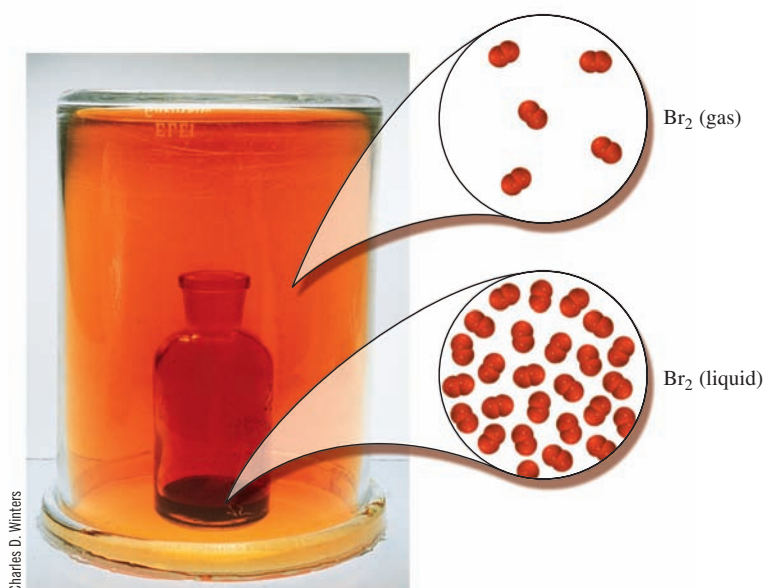
*Variable.

†Atmospheric moisture varies considerably.

► Investigating four variables at once is difficult. In Sections 12-4 through 12-8 we shall see how to study these variables two at a time. Section 12-9 will consolidate these descriptions into a single relationship, the ideal gas equation.

12-3 Pressure

Pressure is defined as force per unit area—for example, pounds per square inch (lb/in^2), commonly known as *psi*. Pressure may be expressed in many different units, as we shall see. The mercury **barometer** is a simple device for measuring atmospheric pressures. Figure 12-1a illustrates the “heart” of the mercury barometer. A glass tube (about 800 mm long) is sealed at one end, filled with mercury, and then carefully inverted into a dish of mercury



Diffusion of bromine vapor in air. Some liquid bromine (dark reddish brown) was placed in the small inner bottle. As some of the liquid evaporated, the resulting reddish brown gas diffused to fill the larger container.

Unless otherwise noted, all content on this page is © Cengage Learning.

without air being allowed to enter. The mercury in the tube falls to the level at which the pressure of the air on the surface of the mercury in the dish equals the gravitational pull downward on the mercury in the tube. The air pressure is measured in terms of the height of the mercury column, that is, the vertical distance between the surface of the mercury in the open dish and that inside the closed tube. The pressure exerted by the atmosphere is equal to the pressure exerted by the column of mercury.

Mercury barometers are simple and well known, so gas pressures are frequently expressed in terms of millimeters of mercury (mm Hg, or just mm). In recent years the unit **torr** has been used to indicate pressure; it is defined as $1 \text{ torr} = 1 \text{ mm Hg}$.

A mercury **manometer** consists of a glass U-tube partially filled with mercury. One arm is open to the atmosphere, and the other is connected to a container of gas (see Figure 12-1b,c).

Atmospheric pressure varies with atmospheric conditions and distance above sea level. The atmospheric pressure decreases with increasing elevation because there is a smaller mass of air above it. Approximately one-half of the matter in the atmosphere is less than 20,000 feet above sea level. Thus, atmospheric pressure is only about one-half as great at 20,000 feet as it is at sea level. Mountain climbers and pilots use portable barometers to determine their altitudes (Figure 12-2). At sea level, at a latitude of 45° , the average atmospheric pressure supports a column of mercury 760 mm high in a simple mercury barometer when the mercury and air are at 0°C . This average sea-level pressure of 760 mm Hg is called one atmosphere of pressure.

► The unit *torr* was named for Evangelista Torricelli (1608–1647), who invented the mercury barometer.

► A common pressure unit used in much of the world is the bar, which is nearly equal to an atmosphere of pressure:

$$\begin{aligned} 1.00 \text{ bar} &= 100. \text{ kPa} \\ 1.00 \text{ atm} &= 1.01 \text{ bar} \end{aligned}$$

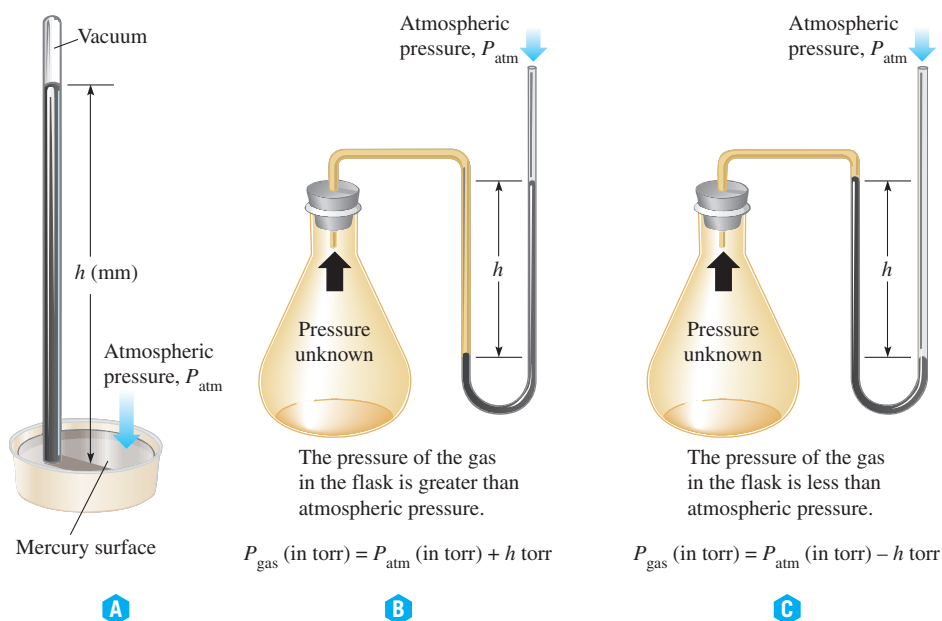


Figure 12-1 Some laboratory devices for measuring pressure. (a) Schematic diagram of a closed-end barometer. At the level of the lower mercury surface, the pressure both inside and outside the tube must be equal to that of the atmosphere. There is no air inside the tube, so the pressure is exerted only by the mercury column h mm high. Hence, the atmospheric pressure must equal the pressure exerted by h mm Hg, or h torr. (b) The two-arm mercury barometer is called a manometer. In this sample, the pressure of the gas inside the flask is *greater than* the external atmospheric pressure. At the level of the lower mercury surface, the total pressure on the mercury in the left arm must equal the total pressure on the mercury in the right arm. The pressure exerted by the gas is equal to the external pressure *plus* the pressure exerted by the mercury column of height h mm, or $P_{\text{gas}} \text{ (in torr)} = P_{\text{atm}} \text{ (in torr)} + h \text{ torr}$. (c) When the gas pressure measured by the manometer is *less than* the external atmospheric pressure, the pressure exerted by the atmosphere is equal to the gas pressure *plus* the pressure exerted by the mercury column, or $P_{\text{atm}} = P_{\text{gas}} + h$. We can rearrange this to write $P_{\text{gas}} \text{ (in torr)} = P_{\text{atm}} \text{ (in torr)} - h \text{ torr}$.



Charles D. Winters

A A commercial mercury barometer



Leonard Lessin/Photo Researchers, Inc

B Portable barometers. This type is called an *aneroid* (“not wet”) barometer. Some of the air has been removed from the airtight box, which is made of thin, flexible metal. When the pressure of the atmosphere changes, the remaining air in the box expands or contracts (Boyle’s Law), moving the flexible box surface and an attached pointer along a scale.



© 1994 Joseph P. Simnot - Fundamental Photographs

C A tire gauge. This kind of gauge registers “relative” pressure, that is, the *difference* between internal pressure and the external atmospheric pressure. For instance, when the gauge reads 30 psi (pounds per square inch), the total gas pressure in the tire is 30 psi + 1 atm, or about 45 psi. In engineering terminology, this is termed “psig” (g = gauge). For all calculations involving pressure, the total pressure, not gauge pressure, must be used.

Figure 12-2 Some commercial pressure-measuring devices.

$$\text{one atmosphere (atm)} = 760 \text{ mm Hg at } 0^\circ\text{C} = 760 \text{ torr}$$

The SI unit of pressure is the **pascal** (Pa), defined as the pressure exerted by a force of one newton acting on an area of one square meter. By definition, one *newton* (N) is the force required to give a mass of one kilogram an acceleration of one meter per second per second. Symbolically we represent one newton as

$$1 \text{ N} = \frac{1 \text{ kg} \cdot \text{m}}{\text{s}^2} \quad \text{so} \quad 1 \text{ Pa} = \frac{1 \text{ N}}{\text{m}^2} = \frac{1 \text{ kg}}{\text{m} \cdot \text{s}^2}$$

One atmosphere of pressure = 1.01325×10^5 Pa, or 101.325 kPa.

► Acceleration is the change in velocity (m/s) per unit time (s), m/s^2 .

12-4 Boyle’s Law: The Volume–Pressure Relationship

Early experiments on the behavior of gases were carried out by Robert Boyle (1627–1691). In a typical experiment (Figure 12-3), a sample of a gas was trapped in a U-tube and allowed to come to constant temperature. Then its volume and the difference in the heights of the two mercury columns were recorded. This difference in height plus the pressure of the atmosphere represents the pressure on the gas. Addition of more mercury to the tube increases the pressure by changing the height of the mercury column. As a result, the gas volume decreases. The results of several such experiments are tabulated in Figure 12-4a.

Boyle showed that for a given sample of gas at constant temperature, the product of pressure and volume, $P \times V$, was always the same number.

Unless otherwise noted, all content on this page is © Cengage Learning.

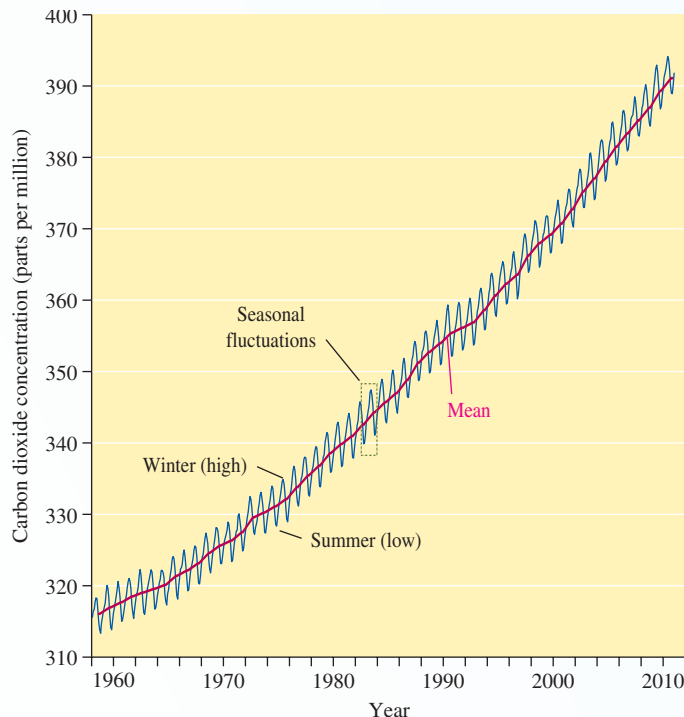
CHEMISTRY IN USE

The Greenhouse Effect and Climate Change

During the 20th century, the great increase in our use of fossil fuels caused a significant rise in the concentration of carbon dioxide, CO_2 , in the atmosphere. Since 1750 (just before the Industrial Revolution), the concentration of atmospheric CO_2 has increased by 37%. Since 2000, acceleration of the annual rate of CO_2 production has increased to more than 3%, from 1.1% per year in the early 1990s. Scientists believe that atmospheric CO_2 concentration could double, compared to 1750, by early in the 21st century. The curve in Figure (a) illustrates the recent steady rise in atmospheric CO_2 concentration.

Energy from the sun reaches the earth in the form of light. Neither CO_2 nor H_2O vapor absorbs the visible light in sunlight, so they do not prevent it from reaching the surface of the earth. The energy given off by the earth in the form of lower-energy infrared (heat) radiation, however, is readily absorbed by CO_2 and H_2O (as it is by the glass or plastic of greenhouses). Thus, some of the heat the earth must lose to maintain its temperature can become trapped in the atmosphere, causing the temperature to rise [Figure (b)]. This phenomenon, called the *greenhouse effect*, has been the subject of much discussion among scientists and the topic of many articles in the popular press.

The Intergovernmental Panel on Climate Change (IPCC) has summarized climate model predictions. The IPCC summary indicates that the average global surface temperature will likely rise an additional 1.1 to 6.4°C (2.0 to 11.5°F) during the 21st century. This may not seem like much. A change of even 4–5°C, however, would be enough to cause a dramatic change in climate, transforming now productive land into desert and altering the habitats of many animals and plants beyond their ability to adapt. Another drastic consequence of even this small temperature rise would be the partial melting of the polar ice caps. The resulting rise in sea level, though only a few feet, would mean that water would inundate coastal cities such as Los Angeles, New York, and Houston, and low-lying coastal areas such as southern Florida and Louisiana. On a global scale, the effects would be devastating.



(a) A plot of the monthly average CO_2 concentration in parts per million (ppm), measured at Mauna Loa Observatory, Hawaii, far from significant sources of CO_2 from human activities. Annual fluctuations occur because plants in the Northern Hemisphere absorb CO_2 in the spring and release it as they decay in the fall.

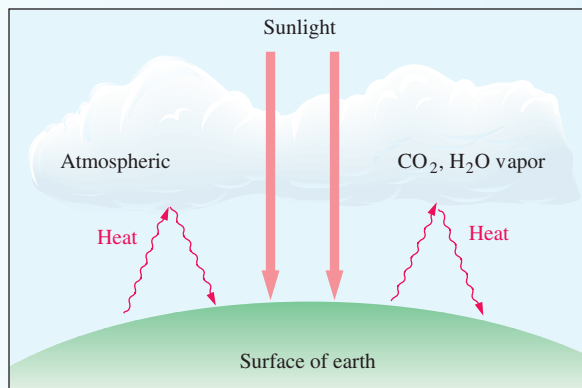
The earth's forests and jungles play a crucial role in maintaining the balance of gases in the atmosphere, removing CO_2 and supplying O_2 . The massive destruction, for economic reasons, of heavily forested areas such as the Amazon rain forest in South America is cited as another long-term contributor to global environmental problems. Worldwide, more than 3 million square miles of once-forested land is now barren for some reason; at least 60% of this land is now unused. Environmental scientists estimate that if even one quarter of this

At a given temperature, the product of pressure and volume of a definite mass of gas is constant.

$$PV = k \quad (\text{constant } n, T)$$

This relationship is **Boyle's Law**. The value of k depends on the amount (number of moles, n) of gas present and on the temperature, T . Units for k are determined by the units used to express the volume (V) and pressure (P).

When the volume of a gas is plotted against its pressure at constant temperature, the resulting curve is one branch of a hyperbola. Figure 12-4b is a graphic illustration of this inverse relationship. When volume is plotted versus the reciprocal of the pressure, $1/P$,



(b) The greenhouse effect. Visible light passes through atmospheric H_2O and CO_2 , but heat radiated from the surface of the earth is absorbed by these gases.

land could be reforested, the vegetation would absorb 1.1 billion tons of CO_2 annually.

Some scientists are more skeptical than others about the role of human-produced CO_2 in climate change and, indeed, about whether global warming is a significant phenomenon or simply another of the recognized warm-cold cycles that have occurred throughout the earth's history. All but the



© AP Photo/Douglas Engle

most skeptical observers, however, seem to agree that responsible stewardship of the planet urgently requires that we do something in a reasoned fashion to reduce production of greenhouse gases, primarily CO_2 , and that this will involve decreasing our dependence on energy from fossil fuels and increasing reliance on renewable energy sources, solar energy, wind power, and geothermal energy. Despite the technical and political problems of waste disposal, increased use of electric energy based on nuclear power is one way of decreasing CO_2 emissions. France, for example, gets 78% of its electricity from nuclear power. Improved ways to recycle the nuclear waste have been developed to minimize the amount needed for long-term storage.

Much CO_2 is eventually absorbed by the vast amount of water in the oceans, where the carbonate-bicarbonate buffer system almost entirely counteracts any adverse effects of ocean water acidity. Ironically, there is also evidence to suggest that other types of air pollution in the form of particulate matter may partially counteract the greenhouse effect. The particles reflect visible (sun) radiation rather than absorbing it, blocking some light from entering the atmosphere. It seems foolish, however, to depend on one form of pollution to help rescue us from the effects of another! Real solutions to current environmental problems such as the greenhouse effect are not subject to quick fixes; they depend on long-term cooperative international efforts that must be based on the firm knowledge resulting from scientific research.

Tropical rain forests are important in maintaining the balance of CO_2 and O_2 in the earth's atmosphere. In recent years a portion of the South American forests (by far the world's largest) larger than France has been destroyed, either by flooding caused by hydroelectric dams or by clearing of forest land for agricultural or ranching use. Such destruction continues at a rate of more than 20,000 square kilometers per year. If current trends continue, many of the world's rain forests will be severely reduced or even obliterated in the next few years. The fundamental question—"What are the long-term consequences of the destruction of tropical rain forests?"—remains unanswered.

a straight line results (see Figure 12-4c). In 1662, Boyle summarized the results of his experiments on various samples of gases in an alternative statement of Boyle's Law:

At constant temperature the volume, V , occupied by a definite mass of a gas is inversely proportional to the applied pressure, P .

$$V \propto \frac{1}{P} \quad \text{or} \quad V = k\left(\frac{1}{P}\right) \quad (\text{constant } n, T)$$

At normal temperatures and pressures, most gases obey Boyle's Law rather well. We call this *ideal behavior*. Deviations from ideality are discussed in Section 12-15.

► The symbol $\propto$ reads "is proportional to." A proportionality is converted into an equality by introducing a proportionality constant, k .

Unless otherwise noted, all content on this page is © Cengage Learning.

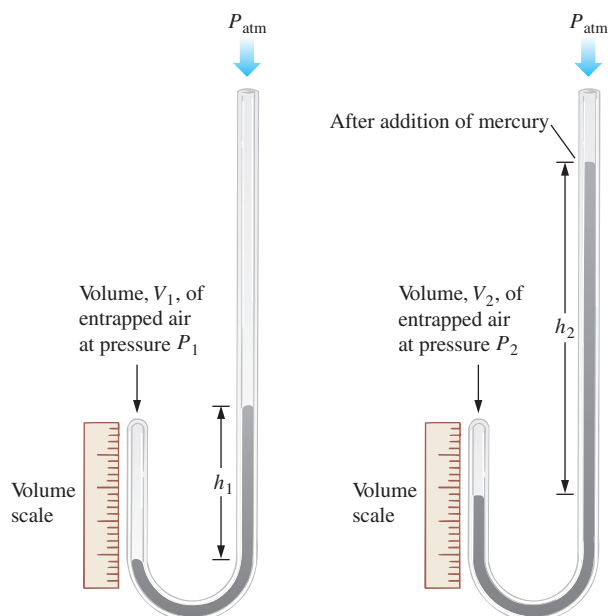
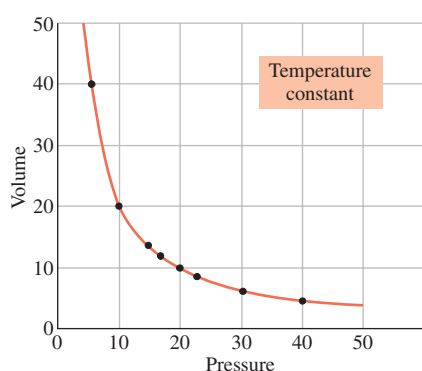


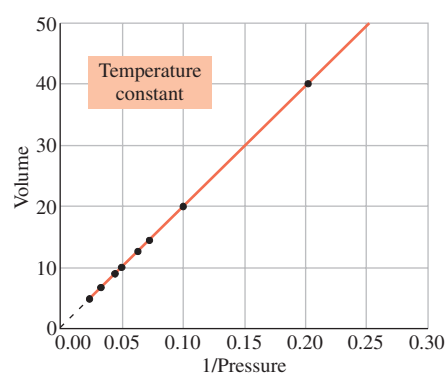
Figure 12-3 A representation of Boyle's experiment. A sample of air is trapped in a tube in such a way that the pressure on the air can be changed and the volume of the air measured. P_{atm} is the atmospheric pressure, measured with a barometer. $P_1 = h_1 + P_{\text{atm}}$, $P_2 = h_2 + P_{\text{atm}}$.

P	V	$P \times V$	$1/P$
5.0	40.0	200	0.20
10.0	20.0	200	0.10
15.0	13.3	200	0.0667
17.0	11.8	201	0.0588
20.0	10.0	200	0.0500
22.0	9.10	200	0.0455
30.0	6.70	201	0.0333
40.0	5.00	200	0.0250

A Some typical data from an experiment such as that shown in Figure 12-3. Measured values of P and V are presented in the first two columns, on an arbitrary scale.



B Graphical representation of Boyle's Law, using the data of (a); V versus P .



C Graphical representation of Boyle's Law, using the data of (a); V versus $1/P$. Although the line would appear to intersect the origin, indicating zero volume when extended to $1/P = 0$ (or infinite pressure), for any real gas the volume levels off at a small but non-zero value at very high pressure.

Figure 12-4 Boyle's Law data and plots of the data.

Let us think about a fixed mass of gas at constant temperature, but at two different conditions of pressure and volume (see Figure 12-3). For the first condition we can write

$$P_1 V_1 = k \quad (\text{constant } n, T)$$

and for the second condition we can write

$$P_2 V_2 = k \quad (\text{constant } n, T)$$

Because the constant k on the right-hand sides of these two equations is the same, the left-hand sides must be equal, or

$$P_1 V_1 = P_2 V_2 \quad (\text{for a given amount of a gas at constant temperature})$$

This form of Boyle's Law is useful for calculations involving pressure and volume *changes*, as the following examples demonstrate.

EXAMPLE 12-1 Boyle's Law Calculation

A sample of gas occupies 12 L under a pressure of 1.2 atm. What would its volume be if the pressure were increased to 2.4 atm?

Plan

We know the volume at one pressure and want to find the volume at another pressure (constant temperature). This suggests that we use Boyle's Law. We tabulate what is known and what is asked for, and then solve the Boyle's Law equation for the unknown quantity, V_2 .

Solution

We have

$$V_1 = 12 \text{ L} \quad P_1 = 1.2 \text{ atm}$$

$$V_2 = ? \quad P_2 = 2.4 \text{ atm}$$

Solving Boyle's Law, $P_1V_1 = P_2V_2$, for V_2 and substituting gives

$$V_2 = \frac{P_1V_1}{P_2} = \frac{(1.2 \text{ atm})(12 \text{ L})}{2.4 \text{ atm}} = 6.0 \text{ L}$$

► It is often helpful to tabulate what is given and what is asked for in a problem.

STOP & THINK

Pressure and volume are inversely proportional. Doubling the pressure halves the volume of a sample of gas at constant temperature.



Problem-Solving Tip Units in Boyle's Law Calculations

"Which units for volume and pressure can be used in Boyle's Law calculations? The units on the two sides of $P_1V_1 = P_2V_2$ must match. Thus you can use *any* volume units—liters, milliliters, cubic feet—and *any* units for pressure—atmospheres, torr, pascals—as long as the *same* units are used on both sides."

EXAMPLE 12-2 Boyle's Law Calculation

A sample of oxygen occupies 10.0 L under a pressure of 790. torr (105 kPa). At what pressure would it occupy 13.4 L if the temperature did not change?

Plan

We know the pressure at one volume and wish to find the pressure at another volume (at constant temperature). We can solve Boyle's Law for the second pressure and substitute.

Solution

We have $P_1 = 790.$ torr; $V_1 = 10.0$ L; $P_2 = ?$; $V_2 = 13.4$ L. Solving Boyle's Law, $P_1V_1 = P_2V_2$, for P_2 and substituting yields

$$P_2 = \frac{P_1V_1}{V_2} = \frac{(790. \text{ torr})(10.0 \text{ L})}{13.4 \text{ L}} = 590. \text{ torr} \left(\times \frac{101.3 \text{ kPa}}{760. \text{ torr}} = 78.6 \text{ kPa} \right)$$

You should now work Exercises 16 and 17.

STOP & THINK

It is a very good idea to think qualitatively about what the answer should be before doing the numerical calculation. For example, since the volume is *increasing*, we should reason qualitatively from Boyle's Law that the pressure must be *decreasing*. This provides a good check on the final numerical answer you calculate.

Problem-Solving Tip Use What You Can Predict About the Answer

In Example 12-1 the calculated volume decrease is consistent with the increase in pressure. This reasoning suggests another method for solving such problems by setting up a “Boyle’s Law factor” to change the volume in the direction required by the pressure change. We reason that the pressure *increase* from 1.2 to 2.4 atm must cause the volume to *decrease* by the factor (1.2 atm/2.4 atm). The solution then becomes

$$\begin{aligned} \underline{?} \text{ L} &= 12 \text{ L} \times (\text{Boyle's Law factor that would decrease the volume}) \\ &= 12 \text{ L} \times \left(\frac{1.2 \text{ atm}}{2.4 \text{ atm}} \right) = 6.0 \text{ L} \end{aligned}$$

Now try solving Example 12-2 using a Boyle’s Law factor.



An artist's representation of Jacques Charles's first ascent in a hydrogen balloon at the Tuileries, Paris, December 1, 1783.

► Lord Kelvin (1824–1907) was born William Thompson. At the age of ten he was admitted to Glasgow University. In 1916, a refrigerator company named its new appliance the Kelvinator, because it was based on Kelvin’s theories.

12-5 Charles’s Law: The Volume–Temperature Relationship; The Absolute Temperature Scale

In his pressure–volume studies on gases, Robert Boyle noticed that heating a sample of gas caused some volume change, but he did not follow up on this observation. About 1800, two French scientists—Jacques Charles (1746–1823) and Joseph Gay-Lussac (1778–1850), pioneer balloonists at the time—began studying the expansion of gases with increasing temperature. Their studies showed that the rate of expansion with increased temperature was constant and was the same for all the gases they studied as long as the pressure remained constant. The implications of their discovery were not fully recognized until many years later. Then scientists used this behavior of gases as the basis of a new temperature scale, the absolute temperature scale.

The change of volume with temperature, at constant pressure, is illustrated in Figure 12-5. From the table of typical data in Figure 12-5b, we see that volume (V , mL) increases as temperature (t , °C) increases, but the quantitative relationship is not yet obvious. These data are plotted in Figure 12-5c (line A), together with similar data for the same gas sample at different pressures (lines B and C).

Lord Kelvin, a British physicist, noticed in 1848 that an extension of the different temperature–volume lines back to zero volume (dashed line) yields a common intercept at -273.15°C on the temperature axis. Kelvin named this temperature **absolute zero**. The degrees on this absolute scale and the Celsius scale are the same size, so 0°C becomes 273.15 degrees above absolute zero. In honor of Lord Kelvin’s work, this scale is called the Kelvin temperature scale. Temperatures on the Kelvin scale are expressed in kelvins (not degrees Kelvin) and represented by K, not °K. As pointed out in Section 1-12, the relationship between the Celsius and Kelvin temperature scales is $K = ^\circ\text{C} + 273.15^\circ$.

If we convert temperatures ($^\circ\text{C}$) to absolute temperatures (K) and plot them using the green scale in Figure 12-5c, the volume–temperature relationship becomes obvious. This relationship is known as **Charles’s Law**.

At constant pressure, the volume occupied by a definite mass of a gas is directly proportional to its absolute temperature.

We can express Charles’s Law in mathematical terms as

$$V \propto T \quad \text{or} \quad V = kT \quad (\text{constant } n, P)$$

Rearranging the expression gives $V/T = k$, a concise statement of Charles’s Law. As the absolute temperature increases, the volume must increase proportionally. If we let

► Absolute zero may be thought of as the limit of thermal contraction for an ideal gas.

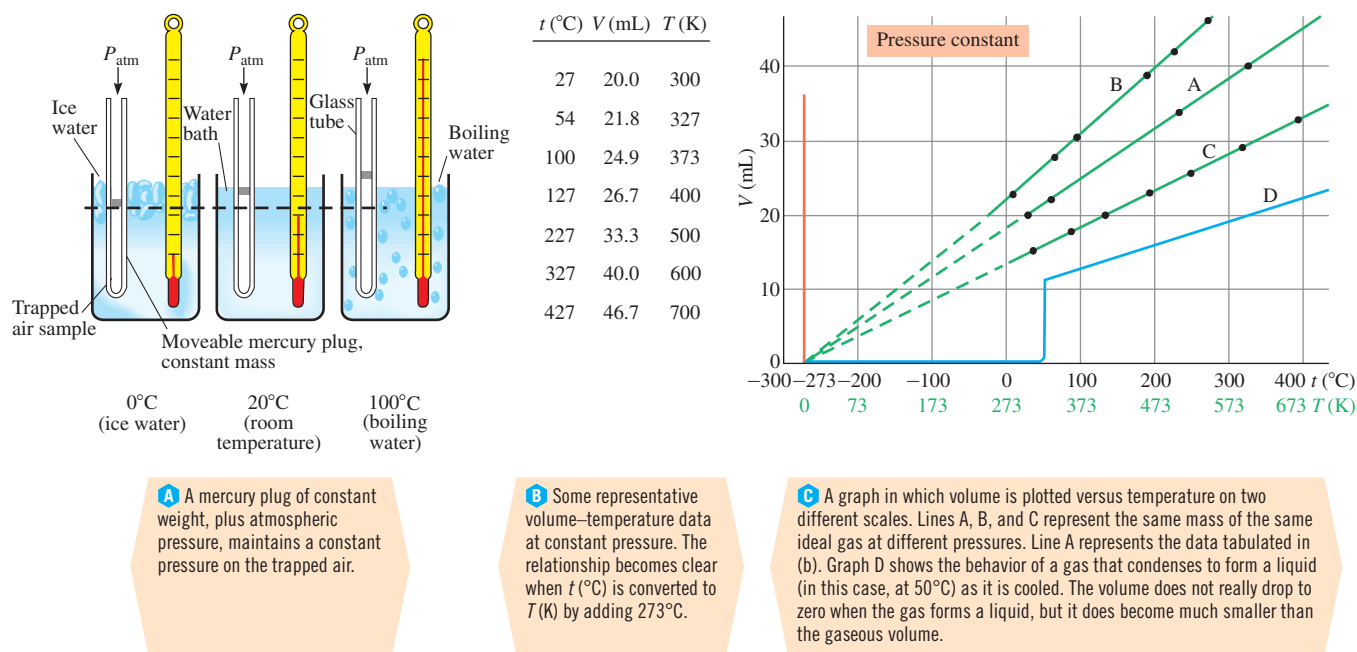


Figure 12-5 An experiment showing that the volume of an ideal gas sample increases as the temperature is increased at constant pressure.

subscripts 1 and 2 represent values for the same sample of gas at two different temperatures, we obtain

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{for a definite mass of gas at constant pressure})$$

which is the more useful form of Charles's Law. This relationship is valid *only* when temperature, T , is expressed on the absolute (Kelvin) scale.

EXAMPLE 12-3 Charles's Law Calculation

A sample of nitrogen occupies 117 mL at 100.°C. At what temperature in °C would it occupy 234 mL if the pressure did not change?

Plan

We know the volume of the sample at one temperature and wish to know its temperature corresponding to a second volume (constant pressure). We can solve Charles's Law for the second temperature. We must remember to carry out calculations with all temperatures expressed on the Kelvin scale, converting to or from Celsius as necessary.

Solution

$$V_1 = 117 \text{ mL} \quad V_2 = 234 \text{ mL}$$

$$T_1 = 100.^\circ\text{C} + 273^\circ = 373 \text{ K} \quad T_2 = ?$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{and} \quad T_2 = \frac{V_2 T_1}{V_1} = \frac{(234 \text{ mL})(373 \text{ K})}{(117 \text{ mL})} = 746 \text{ K}$$

$$^\circ\text{C} = 746 \text{ K} - 273^\circ = 473^\circ\text{C}$$

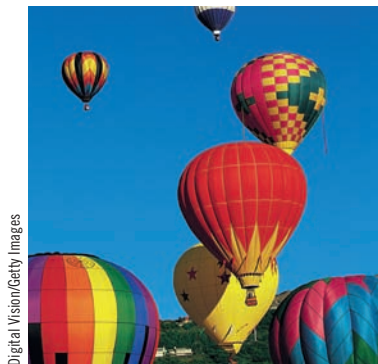
You should now work Exercise 26.

STOP & THINK

You must remember to convert temperatures into kelvins for all gas law calculations. Don't forget to convert the temperature back to the proper units at the end of the problem!

STOP & THINK

To double the volume as required (117 mL to 234 mL), we must double the temperature *on the Kelvin scale* (373 K to 746 K). Note that this does *not* correspond to doubling on the Celsius scale (100°C to 473°C).



Digital Vision/Getty Images

The lower density of the hot air trapped in these balloons causes them to rise in the more dense atmosphere.

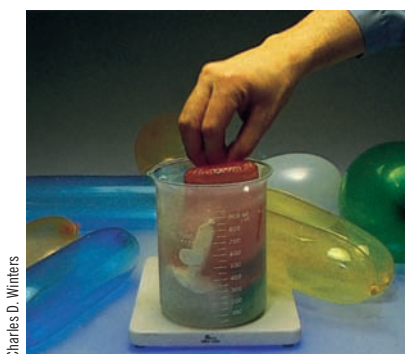


Problem-Solving Tip

Be Careful of Units in Charles's Law Calculations



Which units for volume and temperature are appropriate for Charles's Law calculations? Any volume units—liters, milliliters, cubic feet—can be used as long as the *same* units are used for both volumes. But the relationship *does not apply at all* unless the temperatures are both expressed on an absolute scale. You must remember to express all temperatures in kelvins for Charles's Law calculations.



Charles D. Winters



When balloons filled with air are cooled in liquid nitrogen (bp = -196°C) each shrinks to a small fraction of its original volume. Because the boiling points of the other components of air, except He and Ne, are higher than -196°C , they condense to form liquids. When the balloons are removed from the liquid nitrogen, the liquids vaporize to form gases again. As the air warms to room temperature, the balloons expand to their original volume (Charles's Law).

12-6 Standard Temperature and Pressure

We have seen that both temperature and pressure affect the volumes (and therefore the densities) of gases. It is often convenient to choose some “standard” temperature and pressure as a reference point for discussing gases. **Standard temperature and pressure (STP)** are, by international agreement, exactly 0°C (273.15 K) and one atmosphere of pressure (760. torr).

12-7 The Combined Gas Law Equation

Boyle's Law relates the pressures and volumes of a sample of gas at constant temperature, $P_1V_1 = P_2V_2$. Charles's Law relates the volumes and temperatures at constant pressure, $V_1/T_1 = V_2/T_2$. Combination of Boyle's Law and Charles's Law into a single expression gives the **Combined Gas Law equation**.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad (\text{constant amount of gas})$$

When any five of the variables in the equation are known, the sixth variable can be calculated.

► Notice that the Combined Gas Law equation becomes

1. $P_1V_1 = P_2V_2$ (Boyle's Law)
when T is constant;
2. $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ (Charles's Law)
when P is constant; and
3. $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ when V is constant.

Unless otherwise noted, all content on this page is © Cengage Learning.

EXAMPLE 12-4 Combined Gas Law Calculation

A sample of neon occupies 105 liters at 27°C under a pressure of 985 torr. What volume would it occupy at standard temperature and pressure (STP)?

Plan

All three quantities P , V , and T are changing for this gas sample. This suggests that we use the Combined Gas Law equation. We tabulate what is known and what is asked for, solve the Combined Gas Law equation for the unknown quantity, V_2 , and substitute known values.

Solution

$$\begin{array}{lll} V_1 = 105 \text{ L} & P_1 = 985 \text{ torr} & T_1 = 27^\circ\text{C} + 273^\circ = 300. \text{ K} \\ V_2 = ? & P_2 = 760. \text{ torr} & T_2 = 273 \text{ K} \end{array}$$

Solving for V_2 ,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{so} \quad V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{(985 \text{ torr})(105 \text{ L})(273 \text{ K})}{(760. \text{ torr})(300. \text{ K})} = 124 \text{ L}$$

Alternatively, we can multiply the original volume by a Boyle's Law factor and a Charles's Law factor. As the pressure decreases from 985 torr to 760. torr, the volume increases, so the Boyle's Law factor is 985 torr/760. torr. As the temperature decreases from 300. K to 273 K, the volume decreases, so the Charles's Law factor is 273 K/300. K. Multiplication of the original volume by these factors gives the same result.

$$? \text{ L} = 105 \text{ L} \times \frac{985 \text{ torr}}{760. \text{ torr}} \times \frac{273 \text{ K}}{300. \text{ K}} = 124 \text{ L}$$

EXAMPLE 12-5 Combined Gas Law Calculation

A sample of gas occupies 12.0 liters at 240.°C under a pressure of 80.0 kPa. At what temperature would the gas occupy 15.0 liters if the pressure were increased to 107 kPa?

Plan

The approach is the same as for Example 12-4 except that the unknown quantity is now the new temperature, T_2 .

Solution

$$\begin{array}{lll} V_1 = 12.0 \text{ L} & P_1 = 80.0 \text{ kPa} & T_1 = 240.^\circ\text{C} + 273^\circ = 513 \text{ K} \\ V_2 = 15.0 \text{ L} & P_2 = 107 \text{ kPa} & T_2 = ? \end{array}$$

We solve the Combined Gas Law equation for T_2 .

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{so} \quad T_2 = \frac{P_2 V_2 T_1}{P_1 V_1} = \frac{(107 \text{ kPa})(15.0 \text{ L})(513 \text{ K})}{(80.0 \text{ kPa})(12.0 \text{ L})} = 858 \text{ K}$$

$$\text{K} = ^\circ\text{C} + 273^\circ \quad \text{so} \quad ^\circ\text{C} = 858 \text{ K} - 273^\circ = 585^\circ\text{C}$$

You should now work Exercises 34 and 35.

STOP & THINK

The temperature decrease (from 300. K to 273 K) alone would give only a small *decrease* in the volume of neon, by a factor of 273 K/300. K, or 0.910. The pressure decrease (from 985 torr to 760. torr) alone would result in a greater *increase* in the volume, by a factor of 985 torr/760. torr, or 1.30. The combined result of the two changes is that the volume increases from 105 liters to 124 liters.

STOP & THINK

The pressure is increasing, which would *decrease* the volume; the question asks for a *larger* final volume, so the temperature must increase substantially.

**Problem-Solving Tip** Units in Combined Gas Law Calculations

The Combined Gas Law equation is derived by combining Boyle's and Charles's Laws, so the comments in earlier Problem-Solving Tips also apply to this equation. Remember to express all temperatures in kelvins. Volumes can be expressed in any units as long as both are in the same units. Similarly, any pressure units can be used, so long as both are in the same units. Example 12-4 uses torr for both pressures; Example 12-5 uses kPa for both pressures.

12-8 Avogadro's Law and the Standard Molar Volume

In 1811, Amedeo Avogadro postulated that

at the same temperature and pressure, equal volumes of all gases contain the same number of molecules.

► Small deviations result from the non-ideal behavior of gases

Many experiments have demonstrated that Avogadro's hypothesis is accurate to within about $\pm 2\%$, and the statement is now known as **Avogadro's Law**.

Avogadro's Law can also be stated as follows.

At constant temperature and pressure, the volume, V , occupied by a gas sample is directly proportional to the number of moles, n , of gas.

$$V \propto n \quad \text{or} \quad V = kn \quad \text{or} \quad \frac{V}{n} = k \quad (\text{constant } T, P)$$

For two samples of gas at the same temperature and pressure, the relation between volumes and numbers of moles can be represented as

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad (\text{constant } T, P)$$

The volume occupied by a mole of gas at *standard temperature and pressure*, STP, is referred to as the standard molar volume. It is nearly constant for all gases (Table 12-3).

The **standard molar volume** of an ideal gas is taken to be 22.414 liters per mole at STP.

Table 12-3 Standard Molar Volumes and Densities of Some Gases (0°C)

Gas	Formula	(g/mol)	Density at STP (g/L)	Standard Molar Volume (L/mol)
Hydrogen	H ₂	2.02	0.090	22.428
Helium	He	4.003	0.178	22.426
Neon	Ne	20.18	0.900	22.425
Nitrogen	N ₂	28.01	1.250	22.404
Oxygen	O ₂	32.00	1.429	22.394
Argon	Ar	39.95	1.784	22.393
Carbon dioxide	CO ₂	44.01	1.977	22.256
Ammonia	NH ₃	17.03	0.771	22.094
Chlorine	Cl ₂	70.91	3.214	22.063

► Deviations in standard molar volume indicate that gases do not behave ideally.

Gas densities depend on pressure and temperature; however, the number of moles of gas in a given sample does not change with temperature or pressure. Pressure changes affect volumes of gases according to Boyle's Law, and temperature changes affect volumes of gases according to Charles's Law. We can use these laws to convert gas densities at various temperatures and pressures to *standard temperature and pressure*. Table 12-3 gives the experimentally determined densities of several gases at standard temperature and pressure.

EXAMPLE 12-6 Molecular Weight, Density

One (1.00) mole of a gas occupies 27.0 liters, and its density is 1.41 g/L at a particular temperature and pressure. What is its molecular weight? What is the density of the gas at STP?

Plan

We can use unit factors to convert the density, 1.41 g/L, to molecular weight, g/mol. To calculate the density at STP, we recall that the volume occupied by one mole would be 22.4 L.

Solution

We multiply the density under the original conditions by the unit factor 27.0 L/1.00 mol to generate the appropriate units, g/mol.

$$\frac{? \text{ g}}{\text{mol}} = \frac{1.41 \text{ g}}{\text{L}} \times \frac{27.0 \text{ L}}{\text{mol}} = 38.1 \text{ g/mol}$$

At STP, 1.00 mol of the gas, 38.1 g, would occupy 22.4 L, and its density would be

$$\text{Density} = \frac{38.1 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{22.4 \text{ L}} = 1.70 \text{ g/L at STP}$$

You should now work Exercises 40 and 42.

► Density is defined as mass per unit volume. For solids and liquids this is usually expressed in g/mL, but for gases g/L is more convenient.

STOP & THINK

The appropriate unit factors give the correct units for molecular weight (g/mol) and for density at STP (g/L). The molecular weight is greater than 1, as it must be. The density of a gas is typically much smaller than that of a solid or liquid; these have typical densities on the order of g/mL.

12-9 Summary of Gas Laws: The Ideal Gas Equation

Let us summarize what we have learned about gases. Any sample of gas can be described in terms of its pressure, temperature (in kelvins), volume, and the number of moles, n , present. Any three of these variables determine the fourth. The gas laws we have studied give several relationships among these variables. An **ideal gas** is one that exactly obeys these gas laws. Many gases show slight deviations from ideality, but at normal temperatures and pressures the deviations are usually small enough to be ignored. We will do so for the present and discuss deviations from ideal behavior later.

We can summarize the behavior of ideal gases as follows.

Boyle's Law	$V \propto \frac{1}{P}$	(at constant T and n)
-------------	-------------------------	----------------------------

Charles's Law	$V \propto T$	(at constant P and n)
---------------	---------------	----------------------------

Avogadro's Law	$V \propto n$	(at constant T and P)
----------------	---------------	----------------------------

Summarizing	$V \propto \frac{nT}{P}$	(no restrictions)
-------------	--------------------------	-------------------

As before, a proportionality can be written as an equality by introducing a proportionality constant, for which we use the symbol R . This gives

$$V = R \left(\frac{nT}{P} \right) \quad \text{or, rearranging,} \quad PV = nRT$$

This relationship is called the **ideal gas equation** or the *Ideal Gas Law*. The numerical value of R , the **universal gas constant**, depends on the choices of the units for P , V , and T . One mole of an ideal gas occupies 22.414 liters at 1.0000 atmosphere and 273.15 K (STP). Solving the ideal gas equation for R gives

$$R = \frac{PV}{nT} = \frac{(1.0000 \text{ atm})(22.414 \text{ L})}{(1.0000 \text{ mol})(273.15 \text{ K})} = 0.082057 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

In working problems, we often round R to $0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$.

► This single equation takes into account the values of n , T , P , and V . Restrictions that apply to the individual gas laws are therefore not needed for the ideal gas equation.

STOP & THINK

It is important to use the R value whose units match the pressure and volume units in the problem. We will most commonly use atm and liters as units, but remember to pay attention to what is being used in the problem at hand. As mentioned before, one should always use kelvins for the temperature.

EXAMPLE 12-7 Units of R

R can have any *energy* units per mole per kelvin. Calculate R in terms of joules per mole per kelvin and in SI units of $\text{kPa} \cdot \text{dm}^3/\text{mol} \cdot \text{K}$.

Plan

We apply dimensional analysis to convert to the required units.

Solution

Appendix C shows that $1 \text{ L} \cdot \text{atm} = 101.325 \text{ joules}$.

$$R = \frac{0.082057 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times \frac{101.325 \text{ J}}{1 \text{ L} \cdot \text{atm}} = 8.3144 \text{ J/mol} \cdot \text{K}$$

Now evaluate R in SI units. One atmosphere pressure is 101.325 kilopascals, and the molar volume at STP is 22.414 dm^3 .

$$R = \frac{PV}{nT} = \frac{101.325 \text{ kPa} \times 22.414 \text{ dm}^3}{1 \text{ mol} \times 273.15 \text{ K}} = 8.3145 \frac{\text{kPa} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}}$$

You should now work Exercise 43.

► Recall that $1 \text{ dm}^3 = 1 \text{ L}$.

We can now express R , the universal gas constant, to four digits in three different sets of units.

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} = 8.314 \frac{\text{kPa} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}}$$

We can express R in other units, as shown inside the back cover of this text. Calorie units, for example, are commonly used in science and engineering.

The usefulness of the ideal gas equation is that it relates the four variables, P , V , n , and T , that describe a sample of gas at *one set of conditions*. If any three of these variables are known, the fourth can be calculated.

EXAMPLE 12-8 Ideal Gas Equation

What pressure, in atm, is exerted by 54.0 grams of Xe in a 1.00-liter flask at $20.^\circ\text{C}$?

Plan

We list the variables with the proper units. Then we solve the ideal gas equation for P , substitute values, and evaluate.

Solution

$$V = 1.00 \text{ L} \qquad n = 54.0 \text{ g Xe} \times \frac{1 \text{ mol}}{131.3 \text{ g Xe}} = 0.411 \text{ mol}$$

$$T = 20.^\circ\text{C} + 273^\circ = 293 \text{ K} \qquad P = ?$$

Solving $PV = nRT$ for P and substituting gives

$$P = \frac{nRT}{V} = \frac{(0.411 \text{ mol}) \left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (293 \text{ K})}{1.00 \text{ L}} = 9.89 \text{ atm}$$

STOP & THINK

We are rounding the value of R to three significant figures. The sample is about half a mole of gas, but it is in a much smaller volume than a mole of gas would occupy at or near STP, so it is not surprising that the pressure is much higher than 1 atm.

EXAMPLE 12-9 Ideal Gas Equation

What is the volume of a gas balloon filled with 4.00 moles of He when the atmospheric pressure is 748 torr and the temperature is $30.^\circ\text{C}$?

Plan

We first list the variables with the proper units. Then we solve the ideal gas equation for V , substitute known values, and evaluate.

Solution

$$P = 748 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.984 \text{ atm} \quad n = 4.00 \text{ mol}$$

$$T = 30.^{\circ}\text{C} + 273^{\circ} = 303 \text{ K} \quad V = ?$$

Solving $PV = nRT$ for V and substituting gives

$$V = \frac{nRT}{P} = \frac{(4.00 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (303 \text{ K})}{0.984 \text{ atm}} = 101 \text{ L}$$

You should now work Exercise 46.

STOP & THINK

Remember that 1 mole of gas at 0°C and 760 torr (STP) occupies 22.4 L. Because the pressure in this problem is lower and the temperature a little higher, the volume should be somewhat greater than $4 \times 22.4 \text{ L}$.

You may wonder why pressures are given in torr or mm Hg and temperatures in $^{\circ}\text{C}$. This is because pressures are often measured with mercury barometers, and temperatures are measured with Celsius thermometers.

EXAMPLE 12-10 Ideal Gas Equation

A helium-filled weather balloon has a volume of 7240 cubic feet. How many grams of helium would be required to inflate this balloon to a pressure of 745 torr at 21°C ? ($1 \text{ ft}^3 = 28.3 \text{ L}$)

Plan

We use the ideal gas equation to find n , the number of moles required, and then convert to grams. We must convert each quantity to one of the units stated for R ($R = 0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K}$).

Solution

$$P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}; \quad T = 21^{\circ}\text{C} + 273^{\circ} = 294 \text{ K}$$

$$V = 7240 \text{ ft}^3 \times \frac{28.3 \text{ L}}{1 \text{ ft}^3} = 2.05 \times 10^5 \text{ L}; \quad n = ?$$

Solving $PV = nRT$ for n and substituting gives

$$n = \frac{PV}{RT} = \frac{(0.980 \text{ atm}) (2.05 \times 10^5 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (294 \text{ K})} = 8.32 \times 10^3 \text{ mol He}$$

$$? \text{ g He} = (8.32 \times 10^3 \text{ mol He}) \left(4.00 \frac{\text{g}}{\text{mol}} \right) = 3.33 \times 10^4 \text{ g He}$$

You should now work Exercise 47.



University Corporation for Atmospheric Research

A helium-filled weather balloon.



Problem-Solving Tip Watch Out for Units in Ideal Gas Law Calculations

The units of R that are appropriate for Ideal Gas Law calculations are those that involve units of volume, pressure, moles, and temperature. When you use the value $R = 0.0821 \text{ L} \cdot \text{atm}/\text{mol} \cdot \text{K}$, remember to express all quantities in a calculation in these units. Pressures should be expressed in atmospheres, volumes in liters, temperature in kelvins, and amount of gas in moles. In Examples 12-9 and 12-10 we converted pressures from torr to atm. In Example 12-10 the volume was converted from ft^3 to L.

► Each of the individual gas laws can be derived from the ideal gas equation.

STOP & THINK

When the calculation involves a change in volume, temperature, pressure, or amount of gas, it is more convenient to use one of the individual gas laws. When the calculation does not involve a change in any of these quantities, the ideal gas equation is usually more useful.

Summary of the Ideal Gas Laws

1. The individual gas laws are usually used to calculate the *changes* in conditions for a sample of gas (subscripts can be thought of as “before” and “after”).

Boyle's Law	$P_1V_1 = P_2V_2$	(for a given amount of a gas at constant temperature)
-------------	-------------------	---

Charles's Law	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$	(for a given amount of a gas at constant pressure)
---------------	-------------------------------------	--

Combined Gas Law	$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$	(for a given amount of a gas)
------------------	---	-------------------------------

Avogadro's Law	$\frac{V_1}{n_1} = \frac{V_2}{n_2}$	(for gas samples at the same temperature and pressure)
----------------	-------------------------------------	--

2. The ideal gas equation is used to calculate one of the four variables P , V , n , and T , which describe a sample of gas at *any single set of conditions*.

$$PV = nRT$$

The ideal gas equation can also be used to calculate the densities of gases.

EXAMPLE 12-11 Ideal Gas Equation

Nitric acid, a very important industrial chemical, is made by dissolving the gas nitrogen dioxide, NO_2 , in water. Calculate the density of NO_2 gas, in g/L, at 1.24 atm and $50.^\circ\text{C}$.

Plan

We use the ideal gas equation to find the number of moles, n , in any volume, V , at the specified pressure and temperature. Because we want to express density in g/L, it is convenient to choose a volume of one liter. A different volume could be chosen as long as it is used consistently throughout the solution. Then we convert moles to grams.

Solution

$$V = 1.00 \text{ L} \qquad n = ?$$

$$T = 50.^\circ\text{C} + 273^\circ = 323 \text{ K} \qquad P = 1.24 \text{ atm}$$

Solving $PV = nRT$ for n and substituting gives

$$n = \frac{PV}{RT} = \frac{(1.24 \text{ atm})(1.00 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(323 \text{ K})} = 0.0468 \text{ mol}$$

So there is 0.0468 mol NO_2 in 1.00 L at the specified P and T . Converting this to grams of NO_2 per liter, we obtain

$$\text{Density} = \frac{? \text{ g}}{\text{L}} = \frac{0.0468 \text{ mol NO}_2}{1.00 \text{ L}} \times \frac{46.0 \text{ g NO}_2}{\text{mol NO}_2} = 2.15 \text{ g/L}$$

You should now work Exercise 41.

12-10 Determination of Molecular Weights and Molecular Formulas of Gaseous Substances

In Section 2-9 we distinguished between simplest and molecular formulas of compounds. We showed how simplest formulas can be calculated from percent compositions of compounds. The molecular weight must be known to determine the molecular formula of a compound. For compounds that are gases at convenient temperatures and pressures, the ideal gas law provides a basis for determining molecular weights.

EXAMPLE 12-12 Molecular Weight

A 120.-mL flask contained 0.345 gram of a gaseous compound at 100°C and 760. torr pressure. What is the molecular weight of the compound?

Plan

We use the ideal gas equation, $PV = nRT$, to determine the number of moles of gas that filled the flask. Then, knowing the mass of this number of moles, we can calculate the mass of one mole.

Solution

$$V = 0.120 \text{ L} \quad P = 760. \text{ torr} = 1.00 \text{ atm} \quad T = 100.^{\circ}\text{C} + 273^{\circ} = 373 \text{ K}$$

The number of moles in this gas sample is

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(0.120 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(373 \text{ K})} = 0.00392 \text{ mol}$$

The mass of 0.00392 mol of gas is 0.345 g, so the mass of one mole is

$$\frac{\text{g}}{\text{mol}} = \frac{0.345 \text{ g}}{0.00392 \text{ mol}} = 88.0 \text{ g/mol}$$

You should now work Exercises 55 and 58.

STOP & THINK

Remember to convert °C into K and torr into atm. Then rearrange the ideal gas equation to solve for n , the number of moles.

Let's carry the calculation one step further in the next example.

EXAMPLE 12-13 Molecular Formula

Additional analysis of the gaseous compound in Example 12-12 showed that it contained 54.5% carbon, 9.10% hydrogen, and 36.4% oxygen by mass. What is its molecular formula?

Plan

We first find the simplest formula for the compound as we did in Section 2-8 (Examples 2-13 and 2-14). Then we use the molecular weight that we determined in Example 12-12 to find the molecular formula. To find the molecular formula, we reason as in Example 2-17. We use the experimentally known molecular weight to find the ratio

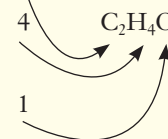
$$n = \frac{\text{molecular weight}}{\text{simplest-formula weight}}$$

The molecular weight is n times the simplest-formula weight, so the molecular formula is n times the simplest formula.

► You may wish to review the calculation of simplest (empirical) formula in Examples 2-13 and 2-14, and the relation between simplest formula and molecular formula in Example 2-17.

Solution

Element	Relative Mass of Element	Relative Number of Atoms (divide mass by AW)	Divide by Smallest Number	Smallest Whole-Number Ratio of Atoms
C	54.5	$\frac{54.5}{12.0} = 4.54$	$\frac{4.54}{2.28} = 1.99$	2
H	9.10	$\frac{9.10}{1.01} = 9.01$	$\frac{9.01}{2.28} = 3.95$	4
O	36.4	$\frac{36.4}{16.0} = 2.28$	$\frac{2.28}{2.28} = 1.00$	1



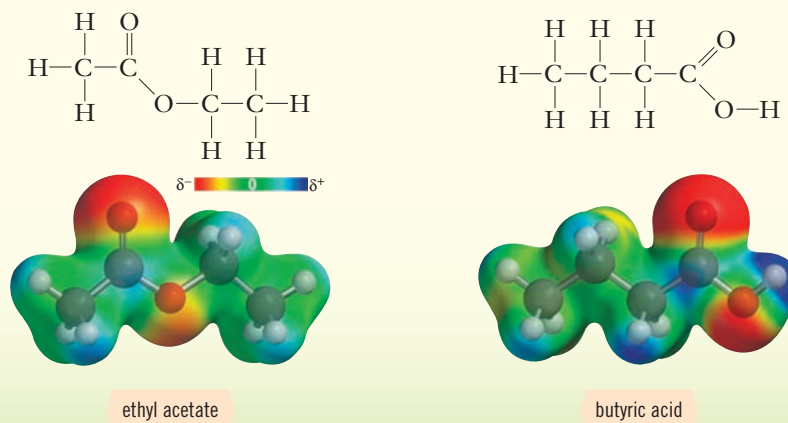
The simplest formula is $\text{C}_2\text{H}_4\text{O}$ and the simplest-formula weight is 44.0 amu.

Division of the molecular weight by the simplest-formula weight gives

$$\frac{\text{molecular weight}}{\text{simplest-formula weight}} = \frac{88.0 \text{ amu}}{44.0 \text{ amu}} = 2$$

The molecular formula is therefore $2 \times (\text{C}_2\text{H}_4\text{O}) = \text{C}_4\text{H}_8\text{O}_2$.

Ethyl acetate and butyric acid are two compounds with this molecular formula. Both have the formula $\text{C}_4\text{H}_8\text{O}_2$. They have very different odors, however. Ethyl acetate has the odor of nail polish remover. Butyric acid has the foul odor of rancid butter.



You should now work Exercise 56.

12-11 Dalton's Law of Partial Pressures

Many gas samples, including our atmosphere, are mixtures that consist of different kinds of gases. The total number of moles in a mixture of gases is

$$n_{\text{total}} = n_{\text{A}} + n_{\text{B}} + n_{\text{C}} + \cdots$$

where n_{A} , n_{B} , and so on represent the number of moles of each kind of gas present. Rearranging the ideal gas equation, $P_{\text{total}}V = n_{\text{total}}RT$, for the total pressure, P_{total} , and then substituting for n_{total} gives

$$P_{\text{total}} = \frac{n_{\text{total}}RT}{V} = \frac{(n_{\text{A}} + n_{\text{B}} + n_{\text{C}} + \cdots)RT}{V}$$

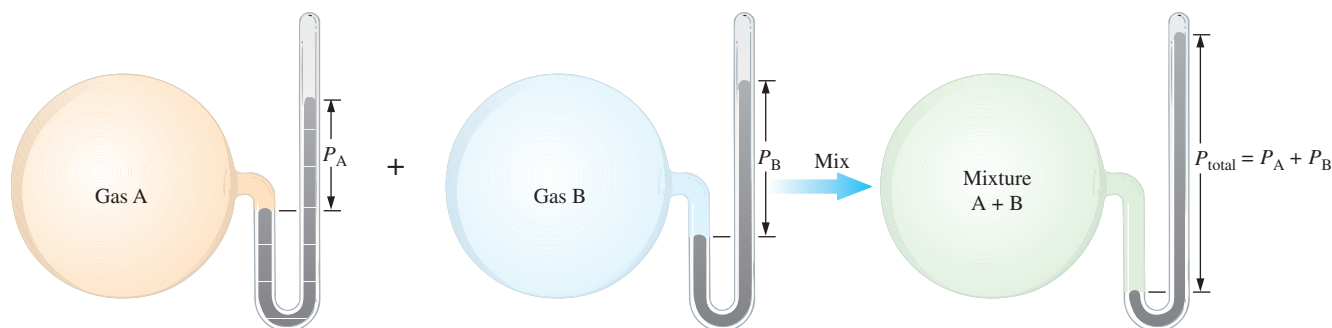


Figure 12-6 An illustration of Dalton's Law. When the two gases A and B are mixed in the same container at the same temperature, they exert a total pressure equal to the sum of their partial pressures.

Multiplying out the right-hand side gives

$$P_{\text{total}} = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V} + \cdots$$

Now $n_A RT/V$ is the *partial pressure* P_A that the n_A moles of gas A alone would exert in the container at temperature T ; similarly, $n_B RT/V = P_B$, and so on. Substituting these into the equation for P_{total} , we obtain **Dalton's Law of Partial Pressures** (Figure 12-6).

$$P_{\text{total}} = P_A + P_B + P_C + \cdots \quad (\text{constant } V, T)$$

The total pressure exerted by a mixture of ideal gases is the sum of the partial pressures of those gases.

Dalton's Law is useful in describing real gaseous mixtures at moderate pressures because it allows us to relate total measured pressures to the composition of mixtures.

► John Dalton was the first to notice this effect. He did so in 1807 while studying the compositions of moist and dry air. The pressure that each gas exerts in a mixture is called its **partial pressure**. No way has been devised to measure the pressure of an individual gas in a mixture; it must be calculated from other quantities.

EXAMPLE 12-14 Mixture of Gases

A 10.0-liter flask contains 0.200 mole of methane, 0.300 mole of hydrogen, and 0.400 mole of nitrogen at 25°C. (a) What is the pressure, in atmospheres, inside the flask? (b) What is the partial pressure of each component of the mixture of gases?

Plan

(a) We are given the number of moles of each component. The ideal gas law can be used to calculate the total pressure from the total number of moles. (b) The partial pressure of each gas in the mixture can be calculated by substituting the number of moles of each gas individually into $PV_A = n_A RT$, $PV_B = n_B RT$, etc.

Solution

$$(a) \quad n_{\text{total}} = 0.200 \text{ mol CH}_4 + 0.300 \text{ mol H}_2 + 0.400 \text{ mol N}_2 = 0.900 \text{ mol of gas}$$

$$V = 10.0 \text{ L} \quad T = 25^\circ\text{C} + 273^\circ = 298 \text{ K}$$

Rearranging $P_{\text{total}}V = n_{\text{total}}RT$ gives $P_{\text{total}} = n_{\text{total}}RT/V$. Substitution gives

$$P_{\text{total}} = \frac{(0.900 \text{ mol}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (298 \text{ K})}{10.0 \text{ L}} = 2.20 \text{ atm}$$

► The gas mixture has a single temperature. Each gas expands to fill the entire volume available.

STOP & THINK

The more moles (n) of a particular gas that are present, the greater the pressure (P) that gas exerts, as predicted by Dalton's Law.

$$n_{\text{N}_2} > n_{\text{H}_2} > n_{\text{CH}_4}$$

so

$$P_{\text{N}_2} > P_{\text{H}_2} > P_{\text{CH}_4}$$

The total pressure is the sum of the pressures exerted by the individual gases.

(b) Now we find the partial pressures. For CH_4 , $n = 0.200$ mol, and the values for V and T are the same as in part (a).

$$P_{\text{CH}_4} = \frac{(n_{\text{CH}_4})RT}{V} = \frac{(0.200 \text{ mol})\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(298 \text{ K})}{10.0 \text{ L}} = 0.489 \text{ atm}$$

Similar calculations for the partial pressures of hydrogen and nitrogen give

$$P_{\text{H}_2} = 0.734 \text{ atm} \quad \text{and} \quad P_{\text{N}_2} = 0.979 \text{ atm}$$

As a check, we use Dalton's Law: $P_{\text{total}} = P_{\text{A}} + P_{\text{B}} + P_{\text{C}} + \dots$. Addition of the partial pressures in this mixture gives the total pressure we calculated in part (a).

$$P_{\text{total}} = P_{\text{CH}_4} + P_{\text{H}_2} + P_{\text{N}_2} = (0.489 + 0.734 + 0.979) \text{ atm} = 2.20 \text{ atm}$$

You should now work Exercises 62 and 63.

► The volume percentages given in Table 12-2 are also equal to mole percentages.

Problem-Solving Tip Amounts of Gases in Mixtures Can Be Expressed in Various Units

In Example 12-14 we were given the number of moles of each gas. Sometimes the amount of a gas is expressed in other units that can be converted to number of moles. For instance, if we know the formula weight (or the formula), we can convert a given mass of gas to number of moles.

We can describe the composition of any mixture in terms of the mole fraction of each component. The **mole fraction**, X_{A} , of component A in a mixture is defined as

$$X_{\text{A}} = \frac{\text{no. mol A}}{\text{total no. mol of all components}}$$

Like any other fraction, mole fraction is a dimensionless quantity. For each component in a mixture, the mole fraction is

$$X_{\text{A}} = \frac{\text{no. mol A}}{\text{no. mol A} + \text{no. mol B} + \dots},$$

$$X_{\text{B}} = \frac{\text{no. mol B}}{\text{no. mol A} + \text{no. mol B} + \dots}, \quad \text{and so on}$$

► The sum of all mole fractions in a mixture is equal to 1.

$$X_{\text{A}} + X_{\text{B}} + \dots = 1 \text{ for any mixture}$$

We can use this relationship to check mole fraction calculations or to find a remaining mole fraction if we know all the others.

For a gaseous mixture, we can relate the mole fraction of each component to its partial pressure as follows. From the ideal gas equation, the number of moles of each component can be written as

$$n_{\text{A}} = P_{\text{A}}V/RT, \quad n_{\text{B}} = P_{\text{B}}V/RT, \quad \text{and so on}$$

and the total number of moles is

$$n_{\text{total}} = P_{\text{total}}V/RT$$

Substituting into the definition of X_{A} ,

$$X_{\text{A}} = \frac{n_{\text{A}}}{n_{\text{A}} + n_{\text{B}} + \dots} = \frac{P_{\text{A}}V/RT}{P_{\text{total}}V/RT}$$

The quantities V , R , and T cancel to give

$$X_A = \frac{P_A}{P_{\text{total}}}; \quad \text{similarly,} \quad X_B = \frac{P_B}{P_{\text{total}}}; \quad \text{and so on}$$

We can rearrange these equations to give another statement of Dalton's Law of Partial Pressures.

$$P_A = X_A \times P_{\text{total}}; \quad P_B = X_B \times P_{\text{total}}; \quad \text{and so on}$$

The partial pressure of each gas in a gaseous mixture is equal to its mole fraction in the mixture times the total pressure of the mixture.

EXAMPLE 12-15 Mole Fraction, Partial Pressure

Calculate the mole fractions of the three gases in Example 12-14.

Plan

One way to solve this problem is to use the numbers of moles given in the problem. Alternatively we could use the partial pressures and the total pressure from Example 12-14.

Solution

Using the moles given in Example 12-14,

$$X_{\text{CH}_4} = \frac{n_{\text{CH}_4}}{n_{\text{total}}} = \frac{0.200 \text{ mol}}{0.900 \text{ mol}} = 0.222$$

$$X_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{total}}} = \frac{0.300 \text{ mol}}{0.900 \text{ mol}} = 0.333$$

$$X_{\text{N}_2} = \frac{n_{\text{N}_2}}{n_{\text{total}}} = \frac{0.400 \text{ mol}}{0.900 \text{ mol}} = 0.444$$

Using the partial and total pressures calculated in Example 12-14,

$$X_{\text{CH}_4} = \frac{P_{\text{CH}_4}}{P_{\text{total}}} = \frac{0.489}{2.20 \text{ atm}} = 0.222$$

$$X_{\text{H}_2} = \frac{P_{\text{H}_2}}{P_{\text{total}}} = \frac{0.734 \text{ atm}}{2.20 \text{ atm}} = 0.334$$

$$X_{\text{N}_2} = \frac{P_{\text{N}_2}}{P_{\text{total}}} = \frac{0.979 \text{ atm}}{2.20 \text{ atm}} = 0.445$$

You should now work Exercise 64.

EXAMPLE 12-16 Partial Pressure, Mole Fraction

The mole fraction of oxygen in the atmosphere is 0.2094. Calculate the partial pressure of O_2 in air when the atmospheric pressure is 760. torr.

Plan

The partial pressure of each gas in a mixture is equal to its mole fraction in the mixture times the total pressure of the mixture.

Solution

$$\begin{aligned} P_{\text{O}_2} &= X_{\text{O}_2} \times P_{\text{total}} \\ &= 0.2094 \times 760. \text{ torr} = 159 \text{ torr} \end{aligned}$$

► Example 12-15 shows that for a gas mixture the relative numbers of moles of components are the same as relative pressures of the components. This is true for all ideal gas mixtures.

STOP & THINK

The more moles (n) of a particular gas that are present, the greater its mole fraction (X) in the mixture.

$$n_{\text{N}_2} > n_{\text{H}_2} > n_{\text{CH}_4}$$

so

$$X_{\text{N}_2} > X_{\text{H}_2} > X_{\text{CH}_4}$$

The difference between the two calculated results is due to rounding.

STOP & THINK

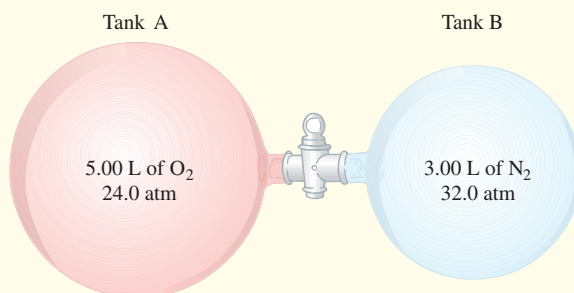
The mole fraction tells us that only a small fraction (about 1/5) of the moles present in air are due to O_2 . Thus the pressure due to O_2 (its partial pressure) must be only that fraction of the total pressure of air (1 atm or 760 torr).

Dalton's Law can be used in combination with other gas laws, as the following example shows.

EXAMPLE 12-17 Mixture of Gases

Two tanks are connected by a closed valve. Each tank is filled with gas as shown, and both tanks are held at the same temperature. We open the valve and allow the gases to mix.

- After the gases mix, what is the partial pressure of each gas, and what is the total pressure?
- What is the mole fraction of each gas in the mixture?



Plan

(a) Each gas expands to fill the available volume, 5.00 liters plus 3.00 liters or a total volume of 8.00 liters. We can use Boyle's Law to calculate the partial pressure that each gas would exert after it expands to fill 8.00 L. The total pressure is equal to the sum of the partial pressures of the two gases. (b) The mole fraction of each gas can be calculated from the ratio of the partial pressure of that gas to the total pressure.

Solution

- (a) For O₂,

$$P_1V_1 = P_2V_2 \quad \text{or} \quad P_{2,\text{O}_2} = \frac{P_1V_1}{V_2} = \frac{24.0 \text{ atm} \times 5.00 \text{ L}}{8.00 \text{ L}} = 15.0 \text{ atm}$$

For N₂,

$$P_1V_1 = P_2V_2 \quad \text{or} \quad P_{2,\text{N}_2} = \frac{P_1V_1}{V_2} = \frac{32.0 \text{ atm} \times 3.00 \text{ L}}{8.00 \text{ L}} = 12.0 \text{ atm}$$

The total pressure is the sum of the partial pressures.

$$P_{\text{total}} = P_{2,\text{O}_2} + P_{2,\text{N}_2} = 15.0 \text{ atm} + 12.0 \text{ atm} = 27.0 \text{ atm}$$

$$(b) \quad X_{\text{O}_2} = \frac{P_{2,\text{O}_2}}{P_{\text{total}}} = \frac{15.0 \text{ atm}}{27.0 \text{ atm}} = 0.556$$

$$X_{\text{N}_2} = \frac{P_{2,\text{N}_2}}{P_{\text{total}}} = \frac{12.0 \text{ atm}}{27.0 \text{ atm}} = 0.444$$

You should now work Exercise 66.

STOP & THINK

Notice that part (b) of this problem has been solved using the mole fraction statement of Dalton's Law, without calculating the number of moles of either gas. As a further check, the sum of the mole fractions is 1.

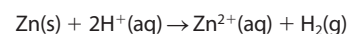
► Gases that are very soluble in water or that react with water cannot be collected by this method. Other liquids can be used.

Some gases can be collected over water. Figure 12-7 illustrates the collection of a sample of hydrogen by displacement of water. A gas produced in a reaction displaces the denser water from the inverted water-filled container. The pressure on the gas inside the collection container could be made equal to atmospheric pressure by collecting gas until the water level inside is the same as that outside.

One complication arises, however. A gas in contact with water soon becomes saturated with water vapor. The pressure inside the container is the sum of the partial pres-



Figure 12-7 Apparatus for preparing hydrogen from zinc and sulfuric acid.



The hydrogen is collected by displacement of water.

sure of the gas itself *plus* the partial pressure exerted by the water vapor in the gas mixture (the **vapor pressure** of water). Every liquid shows a characteristic vapor pressure that varies only with temperature, and *not* with the volume of vapor present, so long as both liquid and vapor are present. Table 12-4 displays the vapor pressure of water near room temperature.

The relevant point here is that a gas collected over water is “moist”; that is, it is saturated with water vapor. Measuring the atmospheric pressure at which the gas is collected, we can write

$$P_{\text{atm}} = P_{\text{gas}} + P_{\text{H}_2\text{O}} \quad \text{or} \quad P_{\text{gas}} = P_{\text{atm}} - P_{\text{H}_2\text{O}}$$

Example 12-18 provides a detailed illustration.

EXAMPLE 12-18 Gas Collected over Water

Hydrogen was collected over water (see Figure 12-7) at 21°C on a day when the atmospheric pressure was 748 torr. The volume of the gas sample collected was 300. mL.

(a) How many moles of H_2 were present? (b) How many moles of water vapor were present in the moist gas mixture? (c) What is the mole fraction of hydrogen in the moist gas mixture? (d) What would be the mass of the gas sample if it were dry?

Plan

(a) The vapor pressure of H_2O , $P_{\text{H}_2\text{O}} = 19$ torr at 21°C, is obtained from Table 12-4. Applying Dalton's Law, $P_{\text{H}_2} = P_{\text{atm}} - P_{\text{H}_2\text{O}}$. We then use the partial pressure of H_2 in the ideal gas equation to find the number of moles of H_2 present. (b) The partial pressure of water vapor (the vapor pressure of water at the stated temperature) is used in the ideal gas equation to find the number of moles of water vapor present. (c) The mole fraction of H_2 is the ratio of its partial pressure to the total pressure. (d) The number of moles found in part (a) can be converted to mass of H_2 .

Solution

$$(a) \quad P_{\text{H}_2} = P_{\text{atm}} - P_{\text{H}_2\text{O}} = (748 - 19) \text{ torr} = 729 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.959 \text{ atm}$$

We also need to convert the volume from mL to L and the temperature to K

$$V = 300. \text{ mL} = 0.300 \text{ L} \quad \text{and} \quad T = 21^\circ\text{C} + 273^\circ = 294 \text{ K}$$

Solving the ideal gas equation for n_{H_2} gives

$$n_{\text{H}_2} = \frac{P_{\text{H}_2}V}{RT} = \frac{(0.959 \text{ atm})(0.300 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(294 \text{ K})} = 1.19 \times 10^{-2} \text{ mol H}_2$$

► The partial pressure exerted by the vapor above a liquid is called the vapor pressure of that liquid. A more extensive table of the vapor pressure of water appears in Appendix E.

Table 12-4 Vapor Pressure of Water Near Room Temperature

Temperature (°C)	Vapor Pressure of Water (torr)
19	16.48
20	17.54
21	18.65
22	19.83
23	21.07
24	22.38
25	23.76
26	25.21
27	26.74
28	28.35

► Remember that *each* gas occupies the *total* volume of the container.

► At STP, this dry hydrogen would occupy 267 mL. Can you calculate this?

$$(b) P_{\text{H}_2\text{O}} = 19 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.025 \text{ atm}$$

V and T have the same values as in Part (a).

$$n_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}V}{RT} = \frac{(0.025 \text{ atm})(0.300 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(294 \text{ K})} = 3.1 \times 10^{-4} \text{ mol H}_2\text{O vapor}$$

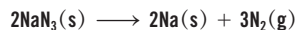
$$(c) X_{\text{H}_2} = \frac{P_{\text{H}_2}}{P_{\text{total}}} = \frac{729 \text{ torr}}{748 \text{ torr}} = 0.975$$

$$(d) \text{? g H}_2 = 1.19 \times 10^{-2} \text{ mol} \times \frac{2.02 \text{ g}}{1 \text{ mol}} = 2.40 \times 10^{-2} \text{ g H}_2$$

You should now work Exercise 68.



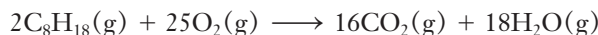
The nitrogen gas formed in the rapid reaction



fills an automobile air bag during a collision. The air bag fills within 1/20th of a second after a front collision.

12-12 Mass–Volume Relationships in Reactions Involving Gases

Many chemical reactions produce gases. For instance, the combustion of hydrocarbon in excess oxygen at high temperatures produces both carbon dioxide and water as gases, as illustrated for octane.



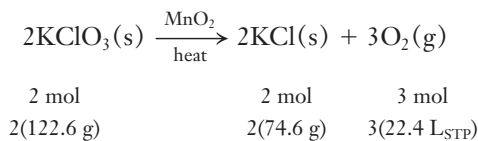
The N_2 gas produced by the very rapid decomposition of sodium azide, $\text{NaN}_3(\text{s})$, inflates air bags used as safety devices in automobiles.

We know that one mole of gas, measured at STP, occupies 22.4 liters; we can use the ideal gas equation to find the volume of a mole of gas at any other conditions. This information can be utilized in stoichiometry calculations (see Section 3-2).

Small amounts of oxygen can be produced in the laboratory by heating solid potassium chlorate, KClO_3 , in the presence of a catalyst, manganese(IV) oxide, MnO_2 . Solid potassium chloride, KCl , is also produced.

CAUTION!

Heating KClO_3 can be dangerous.



The reaction ratio can be constructed as a unit factor using any two of these quantities.

EXAMPLE 12-19 Gas Volume in a Chemical Reaction

What volume of O_2 (STP) could be produced by heating 112 grams of KClO_3 ?

Plan

The preceding equation shows that two moles of KClO_3 produces three moles of O_2 . We construct appropriate unit factors from the balanced equation and the standard molar volume of oxygen to solve the problem.

Solution

$$\begin{aligned}\underline{?} \text{ L}_{\text{STP}} \text{O}_2 &= 112 \text{ g KClO}_3 \times \frac{1 \text{ mol KClO}_3}{122.6 \text{ g KClO}_3} \times \frac{3 \text{ mol O}_2}{2 \text{ mol KClO}_3} \times \frac{22.4 \text{ L}_{\text{STP}} \text{O}_2}{1 \text{ mol O}_2} \\ &= 30.7 \text{ L}_{\text{STP}} \text{O}_2\end{aligned}$$

This calculation shows that the thermal decomposition of 112 grams of KClO_3 produces 30.7 liters of oxygen measured at standard conditions.

You should now work Exercise 80.

EXAMPLE 12-20 Gas Volume in a Chemical Reaction

A 1.80-gram mixture of potassium chlorate, KClO_3 , and potassium chloride, KCl , was heated until all of the KClO_3 had decomposed. After being dried, the liberated oxygen occupied 405 mL at 25°C when the barometric pressure was 745 torr. (a) How many moles of O_2 were produced? (b) What percentage of the mixture was KClO_3 ?

Plan

- (a) The number of moles of O_2 produced can be calculated from the ideal gas equation.
 (b) Then we use the balanced chemical equation to relate the known number of moles of O_2 formed and the mass of KClO_3 that decomposed to produce it.

Solution

(a) $V = 405 \text{ mL} = 0.405 \text{ L}$; $P = 745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.980 \text{ atm}$

$$T = 25^\circ\text{C} + 273^\circ = 298 \text{ K}$$

Solving the ideal gas equation for n and evaluating gives

$$n = \frac{PV}{RT} = \frac{(0.980 \text{ atm})(0.405 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(298 \text{ K})} = 0.0162 \text{ mol O}_2$$

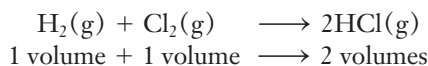
(b) $\underline{?} \text{ g KClO}_3 = 0.0162 \text{ mol O}_2 \times \frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2} \times \frac{122.6 \text{ g KClO}_3}{1 \text{ mol KClO}_3} = 1.32 \text{ g KClO}_3$

The sample contained 1.32 grams of KClO_3 . The percent of KClO_3 in the sample is

$$\% \text{KClO}_3 = \frac{\text{g KClO}_3}{\text{g sample}} \times 100\% = \frac{1.32 \text{ g}}{1.80 \text{ g}} \times 100\% = 73.3\% \text{ KClO}_3$$

You should now work Exercise 84.

Our study of stoichiometry has shown that substances react in definite mole and mass proportions. Using previously discussed gas laws, we can show that gases also react in simple, definite proportions by volume. For example, *one* volume of hydrogen always combines (reacts) with *one* volume of chlorine to form *two* volumes of hydrogen chloride, if all volumes are measured at the same temperature and pressure



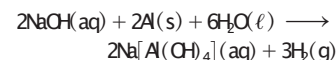
Volumes may be expressed in any units as long as the same unit is used for all. Joseph Louis Gay-Lussac (1778–1850) summarized many experimental observations on combining volumes of gases, leading to **Gay-Lussac's Law of Combining Volumes**:

At constant temperature and pressure, the volumes of gases that react or are formed can be expressed as a ratio of simple whole numbers.



Charles Steele

Production of a gas by a reaction.



This reaction is used in some solid drain cleaners.

STOP & THINK

As before, you will find it especially helpful to express units in complete terms—mol O_2 , mol KClO_3 , g KClO_3 , and g sample.

► Among Gay-Lussac's many contributions to early chemistry were his co-discovery of boron, his thorough report of the properties of the newly discovered iodine, and his development of *volumetric analysis*, in which the volume of a solution of one reactant is used to determine the amount of another reactant.

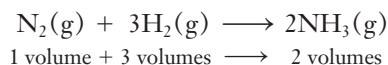
Unless otherwise noted, all content on this page is © Cengage Learning.

► This applies only to *gaseous* substances at the same temperature and pressure. No generalizations can be made about the volumes of solids and liquids as they undergo chemical reactions.

► Mole ratios are equal to volume ratios only for gaseous reactants and products. Gay-Lussac's Law does not apply to any solid or liquid reactants or products that might be present.

The ratio corresponds to the coefficients in the balanced equation for the reaction. Hundreds of examples based on experimental observations could be cited. Here are a few.

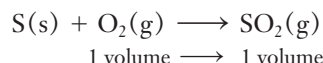
1. One volume of nitrogen can react with three volumes of hydrogen to form two volumes of ammonia



2. One volume of methane reacts with (burns in) two volumes of oxygen to give one volume of carbon dioxide and two volumes of steam



3. Sulfur (a solid) reacts with one volume of oxygen to form one volume of sulfur dioxide



4. Four volumes of ammonia burn in five volumes of oxygen to produce four volumes of nitric oxide and six volumes of steam



12-13 The Kinetic-Molecular Theory

As early as 1738, Daniel Bernoulli (1700–1782) envisioned gaseous molecules in ceaseless motion striking the walls of their container and thereby exerting pressure. In 1857, Rudolf Clausius (1822–1888) published a theory that attempted to explain various experimental observations that had been summarized by Boyle's, Dalton's, Charles's, and Avogadro's laws. The basic assumptions of the **kinetic-molecular theory** for an ideal gas follow.

1. Gases consist of discrete molecules. The individual molecules are very small and are very far apart relative to their own sizes.
2. The gas molecules are in continuous, random, straight-line motion with varying velocities.
3. The collisions between gas molecules and with the walls of the container are elastic; the total energy is conserved during a collision; that is, there is no net energy gain or loss.
4. At any given instant, only a small fraction of the molecules are involved in collisions. Between collisions, the molecules exert no attractive or repulsive forces on one another; instead, each molecule travels in a straight line with a constant velocity.

The observation that gases can be easily compressed indicates that the molecules are far apart. At ordinary temperatures and pressures, the gas molecules themselves occupy an insignificant fraction of the total volume of the container. Near temperatures and pressures at which a gas liquefies, the gas does not behave ideally (see Section 12-15) and attractions or repulsions among gas molecules are significant.

Kinetic energy is the energy a body possesses by virtue of its motion. It is $\frac{1}{2}mu^2$, where m , the body's mass, can be expressed in grams and u , its speed, can be expressed in meters per second (m/s). The assumptions of the kinetic-molecular theory can be used to relate temperature and molecular kinetic energy (see the Enrichment section, pages 431–433).

The *average* kinetic energy of gaseous molecules is directly proportional to the absolute temperature of the sample. The *average* kinetic energies of molecules of different gases are equal at a given temperature.

For instance, the average kinetic energies of the molecules are the same in samples of He, H₂O, N₂, and O₂ at the same temperature. But the lightest molecules, He, have much higher average velocities than do the heavier molecules, H₂O, N₂, and O₂, at the same temperature (Figure 12-8).

We can summarize this very important result from the kinetic-molecular theory.

$$\text{average molecular } KE = \overline{KE} \propto T$$

or

$$\text{average molecular speed} = \bar{u} \propto \sqrt{\frac{T}{\text{molecular weight}}}$$

► A bar over a quantity denotes an *average* of that quantity.

Molecular kinetic energies of gases increase with increasing temperature and decrease with decreasing temperature. We have referred only to the *average* kinetic energy; in a given sample, some molecules are moving quite rapidly while others are moving more slowly. Figure 12-9 shows the distribution of speeds of gaseous molecules at two temperatures.

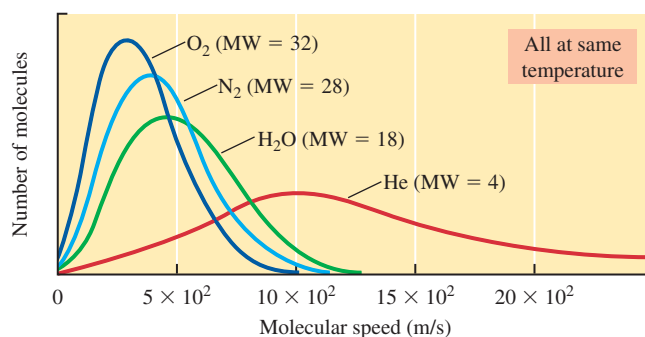


Figure 12-8 The effect of molecular weight on the distribution of molecular speeds at a given temperature. On average, lighter molecules such as He move faster than heavier ones such as O₂.

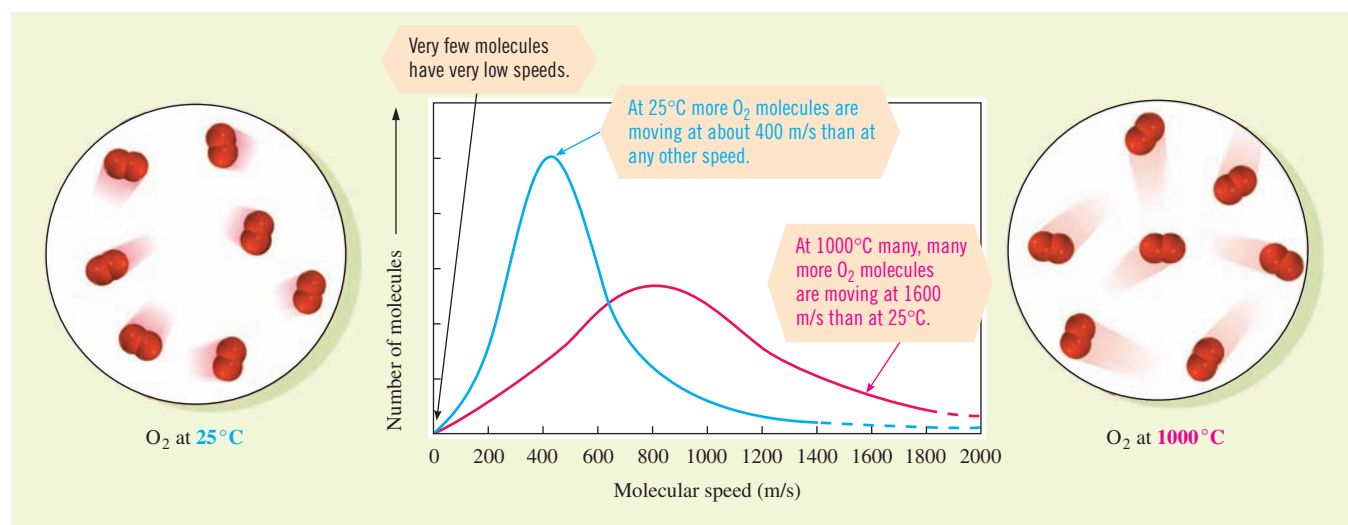


Figure 12-9 The distribution of molecular speeds. This graph shows the relative numbers of O₂ molecules having a given speed at 25°C and at 1000°C. At 25°C, most O₂ molecules have speeds between 200 and 600 m/s (450–1350 miles per hour). Some of the molecules have very high speeds, so the distribution curve approaches the horizontal axis very slowly. The average molecular speed is higher at 1000°C than at 25°C.

► The mathematical description of this distribution of molecular speeds is referred to as the *Maxwell-Boltzmann distribution function*.

Unless otherwise noted, all content on this page is © Cengage Learning.

The kinetic-molecular theory satisfactorily explains most of the observed behavior of gases in terms of molecular behavior. Let's look at the gas laws in terms of the kinetic-molecular theory.

Boyle's Law

The pressure exerted by a gas on the walls of its container is caused by gas molecules striking the walls. Pressure depends on two factors: (1) the number of molecules striking the walls per unit time and (2) how vigorously the molecules strike the walls. If the temperature is held constant, the average speed and the average force of the collisions remain the same. But halving the volume of a sample of gas doubles the pressure because twice as many molecules strike a given area on the walls per unit time. Likewise, doubling the volume of a sample of gas halves the pressure because only half as many gas molecules strike a given area on the walls per unit time (Figure 12-10).

Dalton's Law

In a gas sample the molecules are very far apart and do not attract one another significantly. Each kind of gas molecule acts independently of the presence of the other kind. The molecules of each gas thus collide with the walls with a frequency and vigor that do not change even if other molecules are present (Figure 12-11). As a result, each gas exerts its own partial pressure that is independent of the presence of other gases, and the total pressure is due to the sum of all the molecule-wall collisions.

Figure 12-10 A molecular interpretation of Boyle's Law—the change in pressure of a gas with changes in volume (at constant temperature). The entire apparatus is enclosed in a vacuum. In the smaller volume, more molecules strike the walls per unit time to give a higher pressure.

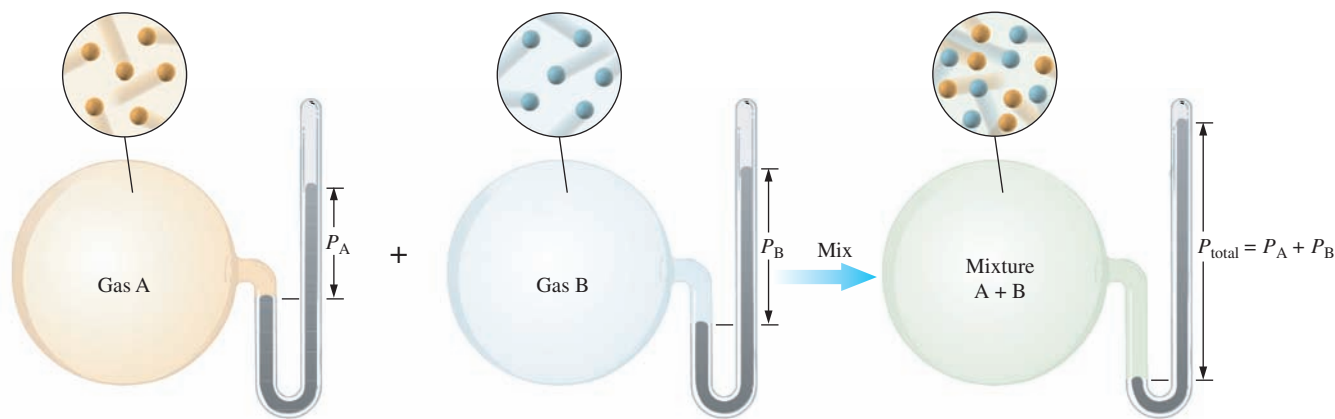
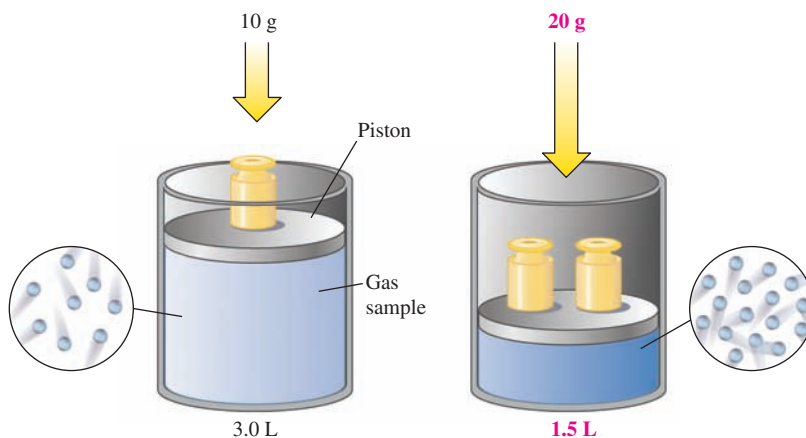


Figure 12-11 A molecular interpretation of Dalton's Law. The molecules act independently in the mixture, so each gas exerts its own partial pressure due to its molecular collisions with the walls. The total gas pressure is the sum of the partial pressures of the component gases.

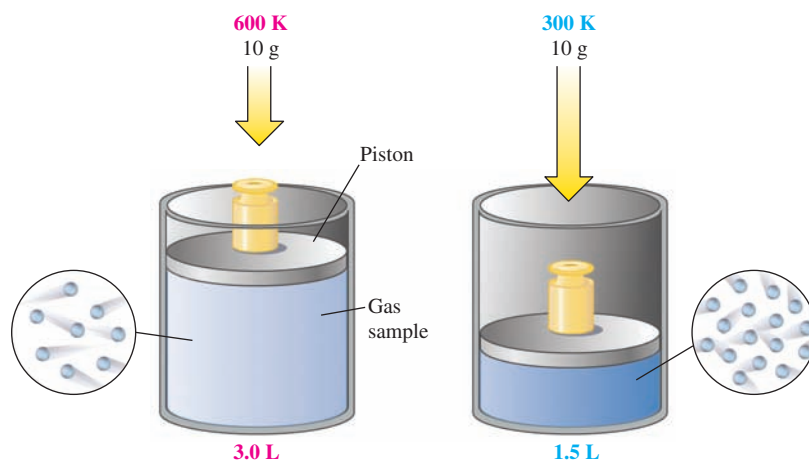


Figure 12-12 A molecular interpretation of Charles's Law—the change in volume of a gas with changes in temperature (at constant pressure). At the lower temperature, molecules strike the walls less often and less vigorously. Thus, the volume must be less to maintain the same pressure.

Charles's Law

Recall that average kinetic energy is directly proportional to the absolute temperature. Doubling the *absolute* temperature of a sample of gas doubles the average kinetic energy of the gaseous molecules, and the increased force of the collisions of molecules with the walls doubles the volume at constant pressure. Similarly, halving the absolute temperature decreases kinetic energy to half its original value; at constant pressure, the volume decreases by half because of the reduced vigor of the collision of gaseous molecules with the container walls (Figure 12-12).

ENRICHMENT

Kinetic-Molecular Theory, the Ideal Gas Equation, and Molecular Speeds

In 1738, Daniel Bernoulli derived Boyle's Law from Newton's laws of motion applied to gas molecules. This derivation was the basis for an extensive mathematical development of the kinetic-molecular theory more than a century later by Clausius, Maxwell, Boltzmann, and others. Although we do not need to study the detailed mathematical presentation of this theory, we can gain some insight into its concepts from the reasoning behind Bernoulli's derivation. Here we present that reasoning based on proportionality arguments.

In the kinetic-molecular theory pressure is viewed as the result of collisions of gas molecules with the walls of the container. As each molecule strikes a wall, it exerts a small impulse. The pressure is the total force thus exerted on the walls divided by the area of the walls. The total force on the walls (and thus the pressure) is proportional to two factors: (1) the impulse exerted by each collision and (2) the rate of collisions (number of collisions in a given time interval).

$$P \propto (\text{impulse per collision}) \times (\text{rate of collisions})$$

Let us represent the mass of an individual molecule by m and its speed by u . The heavier the molecule is (greater m) and the faster it is moving (greater u), the harder it pushes on the wall when it collides. The impulse due to each molecule is proportional to its *momentum*, mu .

$$\text{impulse per collision} \propto mu$$

(continued)

► Recall that momentum is mass $\times$ speed.

(Enrichment, continued)

The rate of collisions, in turn, is proportional to two factors. First, the rate of collision must be proportional to the molecular speed; the faster the molecules move, the more often they reach the wall to collide. Second, this collision rate must be proportional to the number of molecules per unit volume, N/V . The greater the number of molecules, N , in a given volume, the more molecules collide in a given time interval.

$$\text{rate of collisions} \propto (\text{molecular speed}) \times (\text{molecules per unit volume})$$

or

$$\text{rate of collisions} \propto (u) \times \left(\frac{N}{V}\right)$$

We can introduce these proportionalities into the one describing pressure, to conclude that

$$P \propto (mu) \times u \times \frac{N}{V} \quad \text{or} \quad P \propto \frac{Nmu^2}{V} \quad \text{or} \quad PV \propto Nmu^2$$

At any instant not all molecules are moving at the same speed, u . We should reason in terms of the *average* behavior of the molecules, and express the quantity u^2 in average terms as $\overline{u^2}$, the *mean-square speed*.

$$PV \propto Nm\overline{u^2}$$

Not all molecules collide with the walls at right angles, so we must average (using calculus) over all the trajectories. This gives a proportionality constant of $\frac{1}{3}$, and

$$PV = \frac{1}{3} Nm\overline{u^2}$$

This describes the quantity PV (pressure $\times$ volume) in terms of *molecular quantities*—number of molecules, molecular masses, and molecular speeds. The number of molecules, N , is given by the number of moles, n , times Avogadro's number, N_{Av} , or $N = nN_{\text{Av}}$. Making this substitution, we obtain

$$PV = \frac{1}{3} nN_{\text{Av}}m\overline{u^2}$$

The ideal gas equation describes (pressure $\times$ volume) in terms of *measurable quantities*—number of moles and absolute temperature.

$$PV = nRT$$

So we see that the ideas of the kinetic-molecular theory lead to an equation of the same form as the macroscopic ideal gas equation. Thus, the molecular picture of the theory is consistent with the ideal gas equation and gives support to the theory. Equating the right-hand sides of these last two equations and canceling n gives

$$\frac{1}{3} N_{\text{Av}}m\overline{u^2} = RT$$

This equation can also be written as

$$\frac{1}{3} N_{\text{Av}} \times (2 \times \frac{1}{2} m\overline{u^2}) = RT$$

From physics we know that the *kinetic energy* of a particle of mass m moving at speed u is $\frac{1}{2}mu^2$. So we can write

$$\frac{2}{3} N_{\text{Av}} \times (\text{avg KE per molecule}) = RT$$

or

$$N_{\text{Av}} \times (\text{avg KE per molecule}) = \frac{3}{2} RT$$

► $\overline{u^2}$ is the average of the squares of the molecular speeds. It is proportional to the square of the average speed, but the two quantities are not equal.

This equation shows that the absolute temperature is directly proportional to the average molecular kinetic energy, as postulated by the kinetic-molecular theory. Because there are N_{Av} molecules in a mole, the left-hand side of this equation is equal to the total kinetic energy of a mole of molecules.

$$\text{total kinetic energy per mole of gas} = \frac{3}{2}RT$$

With this interpretation, the total molecular-kinetic energy of a mole of gas depends only on the temperature, and not on the mass of the molecules or the gas density.

We can also obtain some useful equations for molecular speeds from the previous reasoning. Solving the equation

$$\frac{1}{2} N_{\text{Av}} m \overline{u^2} = RT$$

for **root-mean-square speed**, $u_{\text{rms}} = \sqrt{\overline{u^2}}$, we obtain

$$u_{\text{rms}} = \sqrt{\frac{3RT}{N_{\text{Av}}m}}$$

We recall that m is the mass of a single molecule. So $N_{\text{Av}}m$ is the mass of Avogadro's number of molecules, or one mole of substance; this is equal to the *molecular weight*, M , of the gas.

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

EXAMPLE 12-21 Molecular Speed

Calculate the root-mean-square speed of H_2 molecules in meters per second at 20°C . Recall that

$$1 \text{ J} = 1 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}$$

Plan

We substitute the appropriate values into the equation relating u_{rms} to temperature and molecular weight. Remember that R must be expressed in the appropriate units.

$$R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} = 8.314 \frac{\text{kg} \cdot \text{m}^2}{\text{mol} \cdot \text{K} \cdot \text{s}^2}$$

Solution

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \frac{\text{kg} \cdot \text{m}^2}{\text{mol} \cdot \text{K} \cdot \text{s}^2} \times 293 \text{ K}}{2.016 \frac{\text{g}}{\text{mol}} \times \frac{1 \text{ kg}}{1000 \text{ g}}}}$$

$$u_{\text{rms}} = \sqrt{3.62 \times 10^6 \text{ m}^2/\text{s}^2} = 1.90 \times 10^3 \text{ m/s (about 4250 mph)}$$

You should now work Exercise 92.

STOP & THINK

As this example illustrates, gas molecules are traveling at very high speeds at most temperatures—the higher the temperature and the lighter the molecules, the faster they travel.

12-14 Diffusion and Effusion of Gases

Because gas molecules are in constant, rapid, random motion, they diffuse quickly throughout any container (Figure 12-13). For example, if hydrogen sulfide (the smell of rotten eggs) is released in a large room, the odor can eventually be detected throughout the room.

► **Effusion** is the escape of a gas through a tiny hole. **Diffusion** of a gas is the movement, due to random molecular motion, of a gas into a space or the mixing of one gas with another.

Unless otherwise noted, all content on this page is © Cengage Learning.

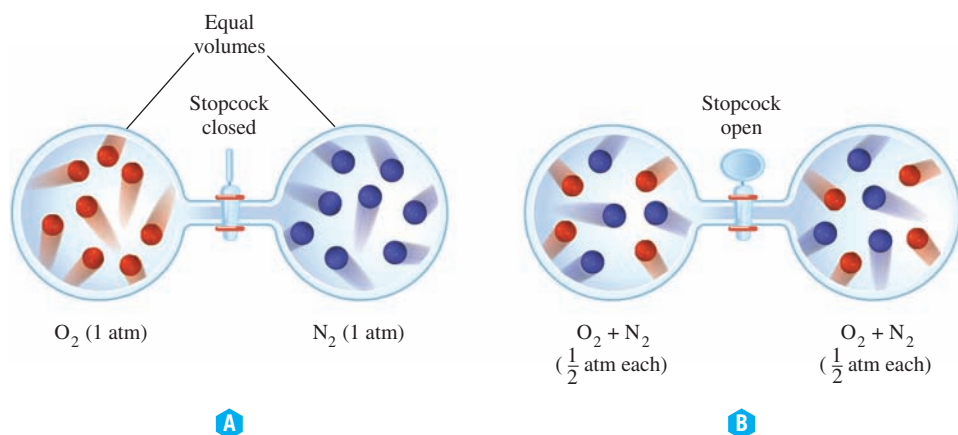


Figure 12-13 A representation of diffusion of gases. The space between the molecules allows for ease of mixing one gas with another. Collisions of molecules with the walls of the container are responsible for the pressure of the gas.

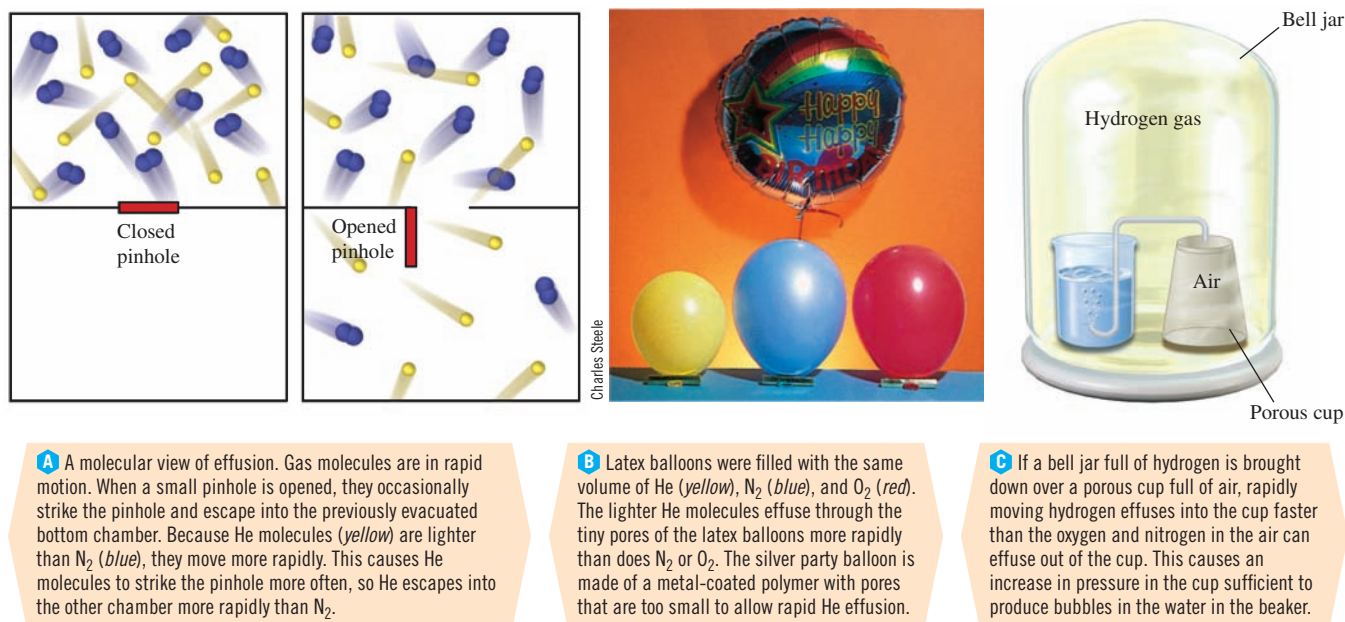
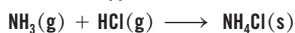


Figure 12-14 Effusion of gases.



NH₃ gas (left) and HCl gas (right) escape from concentrated aqueous solutions. The gases mix and react to form solid ammonium chloride, which appears as a white smoke.



Suggest why the smoke is more prominent nearer the HCl solution.

If a mixture of gases is placed in a container with thin porous walls, the molecules effuse through the walls. Because they move faster, lighter gas molecules effuse through the tiny openings of porous materials faster than heavier molecules (Figure 12-14).

Although they are the most abundant elements in the universe, the gases hydrogen and helium occur only in trace amounts in our atmosphere. This is due to the high average molecular speeds resulting from their low molecular weights. At temperatures in our atmosphere, these molecules reach speeds exceeding the escape velocity required for them to break out of the earth's gravitational pull and diffuse into interplanetary space. Thus, most of the gaseous hydrogen and helium that were probably present in large concentrations in the earth's early atmosphere have long since diffused away. The same is true for the abundance of these gases on other small planets in our solar system, especially those with higher average temperatures than ours (Mercury and Venus). Massive bodies such as stars (including our own sun) are mainly composed of H and He.

12-15 Deviations from Ideal Gas Behavior

Until now our discussions have dealt with *ideal* behavior of gases. By this we mean that the identity of a gas does not affect how it behaves, and the same equations should work equally well for all gases. Under ordinary conditions most gases do behave ideally; their P and V are well described by the ideal gas laws, so they do obey the postulates of the kinetic-molecular theory. According to the kinetic-molecular model, (1) all but a negligible volume of a gas sample is empty space, and (2) the molecules of *ideal* gases do not attract one another because they are so far apart and are considered point masses without any volume.

Under some conditions, however, most gases can have pressures and/or volumes that are *not* accurately predicted by the ideal gas laws. Figure 12-15 illustrates the nonideal behavior of several gases. The ratio of PV/nRT versus pressure should equal 1.0 for an ideal gas. Most gases, however, show marked deviations from ideal behavior at high pressures. This tells us that they are not behaving entirely as postulated by the kinetic-molecular theory.

Nonideal gas behavior (deviation from the predictions of the ideal gas laws) is most significant at *high pressures* and/or *low temperatures*, that is, near the conditions under which the gas liquefies.

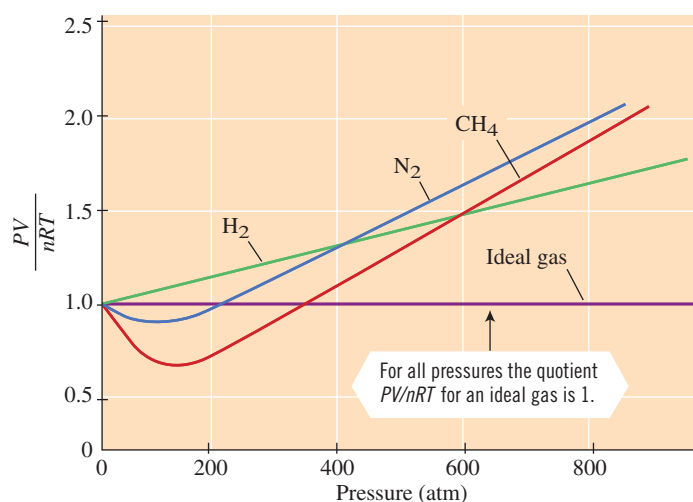
Johannes van der Waals (1837–1923) studied deviations of gases from ideal behavior. In 1867, he empirically adjusted the ideal gas equation

$$P_{\text{ideal}}V_{\text{ideal}} = nRT$$

to take into account two complicating factors.

1. According to the kinetic-molecular theory, the molecules are so small, relative to the total volume of the gas, that each molecule can move through virtually the entire measured volume of the container, V_{measured} (Figure 12-16a). But under high pressures, a gas is compressed so that the volume of the molecules themselves becomes a significant fraction of the total volume occupied by the gas. As a result, the *available volume*, $V_{\text{available}}$, for any molecule to move in is less than the *measured volume* by an amount that depends on the volume excluded by the presence of the other molecules (see Figure 12-16b). To account for this, we subtract a correction factor, nb .

$$V_{\text{available}} = V_{\text{measured}} - nb$$



► The larger the molecular volume, the larger the value of van der Waals' constant b for the gas.

Figure 12-15 Comparison of ideal and nonideal behavior of gases. For a gas that behaves ideally, $PV = nRT$ at all pressures, so $PV/nRT = 1$ at all pressures (*horizontal line*). We can test a gas for ideal behavior by measuring P , V , n , and T for a sample of the gas at various pressures and then calculating PV/nRT . At pressures up to a few atmospheres, all of these plots show PV/nRT near 1, or nearly ideal behavior. Different gases deviate differently from ideal behavior, and these deviations from ideality become more pronounced at higher pressures.

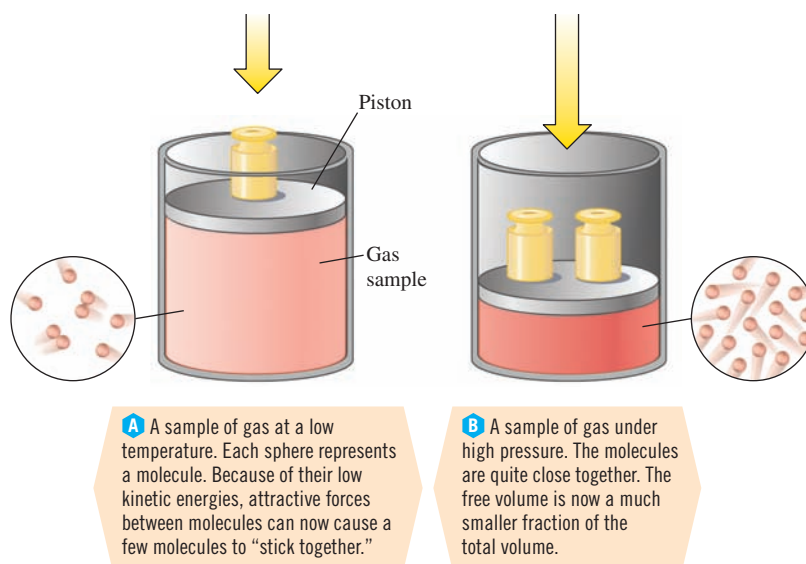


Figure 12-16 A molecular interpretation of deviations from ideal behavior.

The factor nb corrects for the volume occupied by the molecules themselves. Larger molecules have greater values of b , and the greater the number of molecules in a sample (higher n), the larger is the volume correction. The correction term becomes negligibly small, however, when the volume is large (or the pressure is low).

- The kinetic-molecular theory describes pressure as resulting from molecular collisions with the walls of the container; this theory assumes that attractive forces between molecules are insignificant. For any real gas, the molecules can attract one another. But at higher temperatures, the potential energy due to intermolecular attractions is negligibly small compared with the high kinetic energy due to the rapid motion of the molecules and to the great distances between them. When the temperature is quite low (low kinetic energy), the molecules move so slowly that the potential energy due to even small attractive forces *does* become important. This perturbation becomes even more important when the molecules are very close together (at high pressure). As a result of these attractions, the molecules deviate from their straight-line paths and take longer to reach the walls, so fewer collisions take place in a given time interval. Furthermore for a molecule about to collide with the wall, the attraction by its neighbors causes the collision to be less energetic than it would otherwise be (Figure 12-17). As a consequence, the pressure that the gas exerts, P_{measured} , is less than the pressure it would exert if attractions were truly negligible, $P_{\text{ideally exerted}}$. To correct for this, we subtract a correction factor, n^2a/V^2 , from the ideal pressure.

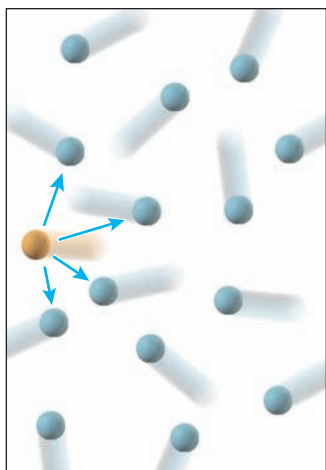


Figure 12-17 A gas molecule strikes the walls of a container with diminished force. The attractive forces between a molecule and its neighbors are significant.

$$P_{\text{measured}} = P_{\text{ideally exerted}} - \frac{n^2a}{V_{\text{measured}}^2}$$

or

$$P_{\text{ideally exerted}} = P_{\text{measured}} + \frac{n^2a}{V_{\text{measured}}^2}$$

In this correction term, large values of a indicate strong attractive forces. When more molecules are present (greater n) and when the molecules are close together (smaller V^2 in the denominator), the correction term becomes larger. The correction term becomes negligibly small, however, when the volume is large.

When we substitute these two expressions for corrections into the ideal gas equation, we obtain the equation

$$\left(P_{\text{measured}} + \frac{n^2 a}{V_{\text{measured}}^2}\right)(V_{\text{measured}} - nb) = nRT$$

or

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

This is the **van der Waals equation**. In this equation, P , V , T , and n represent the *measured* values of pressure, volume, temperature (expressed on the absolute scale), and number of moles, respectively, just as in the ideal gas equation. The quantities a and b are experimentally derived constants that differ for different gases (Table 12-5). When a and b are both zero, the van der Waals equation reduces to the ideal gas equation.

We can understand the relative values of a and b in Table 12-5 in terms of molecular properties. Note that a for helium is very small. This is the case for all noble gases and many other nonpolar molecules, because only very weak attractive forces, called dispersion forces, exist between them. **Dispersion forces** result from short-lived electrical dipoles produced by the attraction of one atom's nucleus for an adjacent atom's electrons. These forces exist for all molecules but are especially important for nonpolar molecules such as N_2 , which lack stronger attractive forces and would never liquefy if dispersion forces did not exist. Polar molecules such as ammonia, NH_3 , have permanent charge separations (dipoles), so they exhibit greater forces of attraction for one another. This explains the high value of a for ammonia. Dispersion forces and permanent dipole forces of attraction are discussed in more detail in Chapter 13.

Larger molecules have greater values of b . For instance, H_2 , a first-row diatomic molecule, has a greater b value than the first-row monatomic He. The b value for CO_2 , which contains three second-row atoms, is greater than that for N_2 , which contains only two second-row atoms.

The following example illustrates the deviation of methane, CH_4 , from ideal gas behavior under high pressure.

► The van der Waals equation, like the ideal gas equation, is known as an *equation of state*, that is, an equation that describes a state of matter.

Table 12-5 van der Waals Constants

Gas	a ($\text{L}^2 \cdot \text{atm}/\text{mol}^2$)	b (L/mol)
H_2	0.244	0.0266
He	0.034	0.0237
N_2	1.39	0.0391
NH_3	4.17	0.0371
CO_2	3.59	0.0427
CH_4	2.25	0.0428

► The larger the intermolecular attraction, the larger the value of van der Waals' constant a for the gas.

EXAMPLE 12-22 van der Waals Equation

Calculate the pressure exerted by 1.00 mole of methane, CH_4 , in a 500.-mL vessel at 25.0°C assuming (a) ideal behavior and (b) nonideal behavior.

Plan

(a) Ideal gases obey the ideal gas equation. We can solve this equation for P . (b) To describe methane as a nonideal gas, we use the van der Waals equation and solve for P .

Solution

(a) Using the ideal gas equation to describe ideal gas behavior,

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{(1.00 \text{ mol})\left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(298 \text{ K})}{0.500 \text{ L}} = 48.9 \text{ atm}$$

(b) Using the van der Waals equation to describe nonideal gas behavior,

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

For CH_4 , $a = 2.25 \text{ L}^2 \text{ atm/mol}^2$ and $b = 0.0428 \text{ L/mol}$ (see Table 12-5).

$$\left[P + \frac{(1.00 \text{ mol})^2 (2.25 \text{ L}^2 \cdot \text{atm/mol}^2)}{(0.500 \text{ L})^2} \right] \left[0.500 \text{ L} - (1.00 \text{ mol}) \left(0.0428 \frac{\text{L}}{\text{mol}} \right) \right] \\ = (1.00 \text{ mol}) \left(\frac{0.0821 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (298 \text{ K})$$

STOP & THINK

The pressure is less than that calculated from the ideal gas law by 4.3 atm (8.8%). A significant error would be introduced by assuming ideal behavior at this high pressure.

Combining terms and canceling units, we get

$$P + 9.00 \text{ atm} = \frac{24.5 \text{ L} \cdot \text{atm}}{0.457 \text{ L}} = 53.6 \text{ atm}$$

$$P = 44.6 \text{ atm}$$

You should now work Exercise 98.

Repeating the calculations of Example 12-22 with the volume twenty times higher ($V = 10.0 \text{ L}$) gives ideal and nonideal pressures, respectively, of 2.45 and 2.44 atm, a difference of only 0.4%.

Many other equations have been developed to describe the nonideal behavior of gases. Each of these equations contains quantities that must be empirically derived for each gas.

KEY TERMS

Absolute zero The zero point on the absolute temperature scale; -273.15°C or 0 K ; theoretically, the temperature at which molecular motion is a minimum.

Atmosphere (atm) A unit of pressure; the pressure that will support a column of mercury 760 mm high at 0°C ; 760 torr.

Avogadro's Law At the same temperature and pressure, equal volumes of all gases contain the same number of molecules.

Bar A unit of pressure; 1.00 bar is equal to 100. kPa (or 0.987 atm).

Barometer A device for measuring atmospheric pressure (see Figures 12-1 and 12-2). The liquid is usually mercury.

Boyle's Law At constant temperature, the volume occupied by a given mass of a gas is inversely proportional to the applied pressure.

Charles's Law At constant pressure, the volume occupied by a definite mass of a gas is directly proportional to its absolute temperature.

Condensed states The solid and liquid states.

Dalton's Law of Partial Pressures The total pressure exerted by a mixture of gases is the sum of the partial pressures of the individual gases.

Diffusion The movement of a substance (e.g., a gas) into a space or the mixing of one substance (e.g., a gas) with another.

Dispersion forces Weak, short-range attractive forces between short-lived temporary dipoles.

Effusion The escape of a gas through a tiny hole or a thin porous wall.

Fluids Substances that flow freely; gases and liquids.

Gay-Lussac's Law of Combining Volumes At constant temperature and pressure, the volumes of gases that react or are formed can be expressed as ratios of small whole numbers.

Ideal gas A hypothetical gas that obeys exactly all postulates of the kinetic-molecular theory.

Ideal gas equation The product of the pressure and volume of an ideal gas is directly proportional to the number of moles of the gas and the absolute temperature.

Kinetic-molecular theory A theory that attempts to explain macroscopic observations of gases in microscopic or molecular terms.

Manometer A two-armed barometer (see Figure 12-1).

Mole fraction The number of moles of a component of a mixture divided by the total number of moles in the mixture.

Partial pressure The pressure exerted by one gas in a mixture of gases.

Pascal (Pa) The SI unit of pressure; it is defined as the pressure exerted by a force of one newton acting on an area of one square meter.

Pressure Force per unit area.

Root-mean-square speed, u_{rms} The square root of the mean-square speed, $\sqrt{\overline{u^2}}$. This is equal to $\sqrt{\frac{3RT}{M}}$ for an ideal gas.

The root-mean-square speed is slightly different from the average speed, but the two quantities are proportional.

Standard molar volume The volume occupied by one mole of an ideal gas under standard conditions, 22.414 liters.

Standard temperature and pressure (STP) Standard temperature 0°C (273.15 K), and standard pressure, one atmosphere, are standard conditions for gases.

Torr A unit of pressure; the pressure that will support a column of mercury 1 mm high at 0°C .

Universal gas constant R , the proportionality constant in the ideal gas equation, $PV = nRT$.

van der Waals equation An equation of state that extends the ideal gas law to real gases by inclusion of two empirically determined parameters, which are different for different gases.

Vapor A gas formed by boiling or evaporation of a liquid or sublimation of a solid; a term commonly used when some of the liquid or solid remains in contact with the gas.

Vapor pressure The pressure exerted by a vapor in equilibrium with its liquid or solid.

EXERCISES

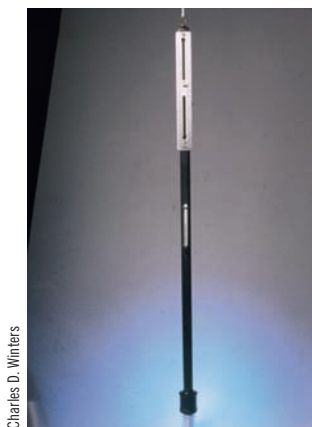
● Molecular Reasoning exercises

▲ More Challenging exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Basic Ideas

1. ● Define pressure. Give a precise scientific definition—one that can be understood by someone without any scientific training.
2. State whether each property is characteristic of all gases, some gases, or no gas: (a) transparent to light; (b) colorless; (c) unable to pass through filter paper; (d) more difficult to compress than liquid water; (e) odorless; (f) settles on standing.
3. Describe the mercury barometer. How does it work?



Charles D. Winters

Barometer

4. What is a manometer? How does it work?
5. Express a pressure of 675 torr in the following units: (a) mm Hg; (b) atm; (c) Pa; (d) kPa.
6. A typical laboratory atmospheric pressure reading is 742 torr. Convert this value to (a) psi, (b) cm Hg, (c) inches Hg, (d) kPa, (e) atm, and (f) ft H₂O.
7. Complete the following table.

	atm	torr	Pa	kPa
Standard atmosphere	1			
Partial pressure of nitrogen in the atmosphere		593		
A tank of compressed hydrogen			1.61×10^5	
Atmospheric pressure at the summit of Mt. Everest				33.7

8. State whether each of the following samples of matter is a gas. If the information is insufficient for you to decide, write “insufficient information.” (a) A material is in a steel tank at 100. atm pressure. The density of the content is uniform throughout. When the tank is opened to the atmosphere, the material immediately

expands, increasing its volume many-fold. (b) A material, on being emitted from an industrial smokestack, rises about 10 m into the air. Viewed against a clear sky, it has a white appearance. (c) 1.0 mL of material weighs 8.2 g. (d) When a material is released from a point 30 ft below the level of a lake at sea level (equivalent in pressure to about 76 cm of mercury), it rises rapidly to the surface, at the same time increasing its volume. (e) A material is transparent and pale green in color. (f) One cubic meter of a material contains as many molecules as 1 m³ of air at the same temperature and pressure.

9. ▲ The densities of mercury and corn oil are 13.5 g/mL and 0.92 g/mL, respectively. If corn oil were used in a barometer, what would be the height of the column, in meters, at standard atmospheric pressure? (The vapor pressure of the oil is negligible.)
10. Steel tanks for storage of gases are capable of withstanding pressures greater than 150. atm. Express this pressure in psi.
11. Automobile tires are normally inflated to a pressure of 33 psi as measured by a tire gauge. (a) Express this pressure in atmospheres. (b) Assuming standard atmospheric pressure, calculate the internal pressure of the tire.



© David J. Greco/Alamy

Tire gauge

Boyle's Law: The Pressure–Volume Relationship

12. (a) On what kinds of observations (measurements) is Boyle's Law based? State the law. (b) Use the statement of Boyle's Law to derive a simple mathematical expression for Boyle's Law.
13. ● Could the words “a fixed number of moles” be substituted for “a definite mass” in the statement of Boyle's Law? Explain.
14. A gas sample contained in a cylinder equipped with a moveable piston occupied 300. mL at a pressure of 2.00 atm. What would be the final pressure if the volume were increased to 567 mL at constant temperature?
15. A balloon that contains 1.50 liters of air at 1.00 atm is taken under water to a depth at which the pressure is 2.50 atm. Calculate the new volume of the balloon. Assume that the temperature remains constant.

● Molecular Reasoning exercises

▲ More Challenging exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

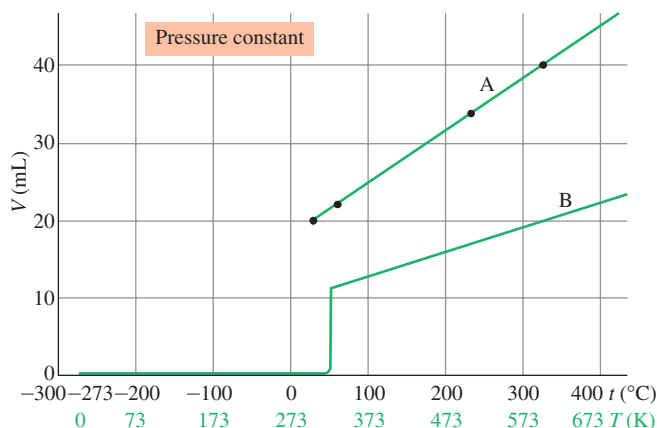
16. A 35.0-L sample of gas collected in the upper atmosphere at a pressure of 59.4 torr is compressed into a 150.-mL container at the same temperature. (a) What is the new pressure, in atmospheres? (b) To what volume would the original sample have had to be compressed to exert a pressure of 10.0 atm?
17. A sample of krypton gas occupies 95.0 mL at 0.500 atm. If the temperature remained constant, what volume would the krypton occupy at (a) 5.00 atm, (b) 0.0500 atm, (c) 555 torr, (d) 5.00 torr, and (e) 5.5×10^{-2} torr?
18. ▲ A cylinder containing 10.0 L of helium gas at a pressure of 165 atm is to be used to fill toy balloons to a pressure of 1.1 atm. Each inflated balloon has a volume of 2.5 L. What is the maximum number of balloons that can be inflated? (Remember that 10.0 L of helium at 1.1 atm will remain in the “exhausted” cylinder.)

Charles's Law: The Volume–Temperature Relationship

19. (a) Can an absolute temperature scale based on Fahrenheit rather than Celsius degrees be developed? Why? (b) Can an absolute temperature scale that is based on a “degree” twice as large as a Celsius degree be developed? Why?
20. (a) What does “absolute temperature scale” mean? (b) Describe the experiments that led to the evolution of the absolute temperature scale. What is the relationship between the Celsius and Kelvin temperature scales? (c) What does “absolute zero” mean?
21. Complete the table by making the required temperature conversions. Pay attention to significant figures.

	Temperature		
	K	°C	°F
Normal boiling point of water		100	
Reference for thermodynamic data	298.15		
Dry ice becomes a gas at atmospheric pressure		−78.5	
The center of the sun (estimated)	1.53×10^7		

Exercises 22 and 24 refer to the plot at the top of the next column. In this figure line A is the plot of volume of a gas versus temperature at a constant pressure for an ideal gas and line B is a plot of the actual behavior of a gas.



22. (a) Why is a plot of volume versus temperature at constant pressure, such as the preceding plot, a straight line? (b) On what kind of observations (measurements) is Charles's Law based? State the law.
23. A sample of air is originally at 32°C. If P and n are kept constant, to what temperature must the air be cooled to (a) decrease its volume by 25%? (b) decrease its volume to 25% of its original volume?
24. Why does the volume drop to nearly zero at about 50°C on line B? Does this gas show ideal behavior at temperatures above 50°C? Would all gases show similar behavior?
25. A gas occupies a volume of 31.0 L at 19.0°C. If the gas temperature rises to 38.0°C at constant pressure, (a) would you expect the volume to double to 62.0 L? Explain. Calculate the new volume (b) at 38.0°C, (c) at 400. K, and (d) at 0°C.
26. Several balloons are inflated with helium to a volume of 0.82 L at 26°C. One of the balloons was found several hours later; the temperature had dropped to 21°C. What would be the volume of the balloon when found, if no helium has escaped?

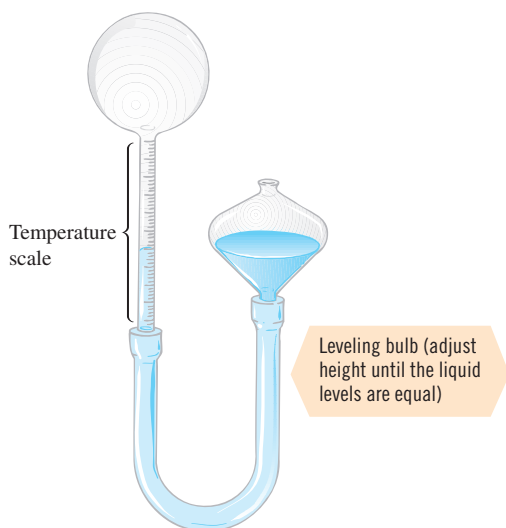


Balloons at different temperatures

27. Which of the following statements are true? Which are false? Why is each true or false? *Assume constant pressure* in each case. (a) If a sample of gas is heated from 100°C to 200°C, the volume will double. (b) If a sample of gas is heated from 0.°C to 273°C, the volume will double. (c) If a sample of gas is cooled from 1273°C to 500.°C, the volume will decrease by a factor of 2. (d) If a sample of gas is cooled

from $100.^{\circ}\text{C}$ to $200.^{\circ}\text{C}$, the volume will decrease by a factor of 5. (e) If a sample of gas is heated from 473°C to 1219°C , the volume will increase by a factor of 2.

28. ▲ The device shown here is a gas thermometer. (a) At the ice point, the gas volume is 1.400 L. What would be the new volume if the gas temperature were raised from the ice point to 8.0°C ? (b) Assume the cross-sectional area of the graduated arm is 1.0 cm^2 . What would be the difference in height if the gas temperature changed from 0°C to 8.0°C ? (c) What modifications could be made to increase the sensitivity of the thermometer?



29. A weather balloon is filled to the volume of 135. L on a day when the temperature is 21°C . If no gases escaped, what would be the volume of the weather balloon after it rises to an altitude where the temperature is -4°C ?
30. Calculate the volume of an ideal gas at the temperatures of dry ice (-78.5°C), liquid N_2 (-195.8°C), and liquid He (-268.9°C) if it occupies 5.00 L at 25.0°C . Assume constant pressure. Plot your results, and extrapolate to zero volume. At what temperature would zero volume be theoretically reached?

The Combined Gas Law

31. Classify the relationship between the variables (a) P and V , (b) V and T , and (c) P and T as either (i) directly proportional or (ii) inversely proportional.
32. Prepare sketches of plots of (a) P versus V , (b) P versus $1/V$, (c) V versus T , and (d) P versus T for an ideal gas.
33. A sample of gas occupies 363. mL at STP. Under what pressure would this sample occupy 236. mL if the temperature were increased to 819°C ?
34. A 385-mL sample of neon exerts a pressure of 670. torr at 26°C . At what temperature in $^{\circ}\text{C}$ would it exert a pressure of 940. torr in a volume of 560. mL?
35. A 256-mL sample of a gas exerts a pressure of 2.75 atm at 16.0°C . What volume would it occupy at 1.00 atm and $100.^{\circ}\text{C}$?

36. Show how Boyle's and Charles's gas laws can be obtained from the combined gas law equation.

STP, Standard Molar Volume, and Gas Densities

37. ● How many molecules of an ideal gas are contained in a 2.50-L flask at STP?
38. ● (a) What is Avogadro's Law? What does it mean? (b) What does "standard molar volume" mean? (c) Does "standard molar volume" refer to liquids and solids as well as gases? (d) Are there conditions other than STP at which 1 mole of an ideal gas would occupy 22.4 L? Explain.
39. ● Using a ground-based telescope and a spectrometer, it has been found that sodium vapor is a significant component of the thin atmosphere of Mercury. Its concentration is estimated to be about 1.0×10^5 atoms per cm^3 . (a) Express this in moles per liter. (b) The maximum temperature of the atmosphere was measured by Mariner 10 to be about $970.^{\circ}\text{C}$. What is the approximate partial pressure of sodium vapor at that temperature?



The surface of the planet Mercury

40. ● Ethylene dibromide (EDB) was formerly used as a fumigant for fruits and grains, but now it is banned because it is a potential health hazard. EDB is a liquid that boils at 109°C . Its molecular weight is 188 g/mol. Calculate its density as a gas at 165°C and 1.00 atm.
41. ● Nitrogen is slightly less dense than is a sample of air at the same temperature and pressure. Calculate the density of N_2 , in g/L, at 1.25 atm and 35°C . If the average molecular weight of the air is 29.2, what is the density of air at the same conditions?
42. ● A laboratory technician forgot what the color coding on some commercial cylinders of gas meant but remembered that each of two specific tanks contained one of the following gases: He, Ne, Ar, or Kr. Measurements at STP made on samples of the gases from the two cylinders showed the gas densities to be 3.74 g/L and 0.900 g/L. (a) Determine by calculation which of these gases was present in each tank. (b) Could this determination be made if the densities had been at a temperature and pressure different from STP?



Molecular Reasoning exercises



More Challenging exercises

Blue-Numbered

exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

The Ideal Gas Equation

43. Calculate R in $\text{L} \cdot \text{atm}/\text{mol} \cdot \text{K}$, in $\text{kPa} \cdot \text{dm}^3/\text{mol} \cdot \text{K}$, in $\text{J}/\text{mol} \cdot \text{K}$, and in $\text{kJ}/\text{mol} \cdot \text{K}$.
44. (a) What is an ideal gas? (b) What is the ideal gas equation? (c) Outline the logic used to obtain the ideal gas equation. (d) What is R ? How can it be derived?
45. (a) A chemist is preparing to carry out a reaction at high pressure that requires 36.0 mol of hydrogen gas. The chemist pumps the hydrogen into a 12.3-L rigid steel container at 25°C. To what pressure (in atmospheres) must the hydrogen be compressed? (b) What would be the density of the high-pressure hydrogen?
46. Calculate the pressure needed to contain 2.54 mol of an ideal gas at 45°C in a volume of 12.75 L.
47. (a) How many molecules are in a 500.-mL container of gaseous oxygen if the pressure is 2.50×10^{-7} torr and the temperature is 1225 K? (b) How many grams of oxygen are in the container?
48. A barge containing 565 tons of liquid chlorine was involved in an accident. (a) What volume would this amount of chlorine occupy if it were all converted to a gas at 750. torr and 18°C? (b) Assume that the chlorine is confined to a width of 0.500 mile and an average depth of 60. ft. What would be the length, in feet, of this chlorine “cloud”?
49. A piece of dry ice ($\text{CO}_2(s)$) has a mass of 22.50 g. It is dropped into an evacuated 2.50-L flask. What is the pressure in the flask at -4°C ?
50. What mass of helium, in grams, is required to fill a 5.0-L balloon to a pressure of 1.1 atm at 25°C?
51. What is the pressure exerted by 1.55 g Xe gas at 20.°C in a 560-mL flask?
52. The standard molar volume of an ideal gas is 22.414 liters per mole at STP. However, the standard molar volume of a gas that has a high molecular weight or strong intermolecular attractive forces can deviate significantly from this value. Calculate the standard molar volume of sulfur hexafluoride (SF_6), density = 6.65 g/L at STP, and hydrogen fluoride (HF), density = 0.922 g/L at STP.
56. A cylinder was found in a storeroom of a manufacturing plant. The label on the cylinder was gone, and no one remembered what the cylinder held. A 0.00500-gram sample was found to occupy 4.13 mL at 23°C and 745 torr. The sample was also found to be composed of only carbon and hydrogen. Identify the gas.
57. A sample of porous rock was brought back from the planet Farout on the other side of the galaxy. Trapped in the rock was a carbon-oxygen gas. The unknown gas was extracted and evaluated. A volume of 3.70 mL of the gas was collected under the conditions of STP. The mass of the gas sample was determined to be 0.00726 grams. Additional analysis proved that there was only one compound present in the gas sample. What was the most probable identity of the gas based on these analyses?
58. A highly volatile liquid was allowed to vaporize completely into a 250.-mL flask immersed in boiling water. From the following data, calculate the molecular weight (in amu per molecule) of the liquid. Mass of empty flask = 65.347 g; mass of flask filled with water at room temperature = 327.4 g; mass of flask and condensed liquid = 65.739 g; atmospheric pressure = 743.3 torr; temperature of boiling water = 99.8°C; density of water at room temperature = 0.997 g/mL.
59. A pure gas contains 85.63% carbon and 14.37% hydrogen by mass. Its density is 2.50 g/L at STP. What is its molecular formula?

Gas Mixtures and Dalton's Law

60. (a) What are partial pressures of gases? (b) State Dalton's Law. Express it symbolically.
61. A sample of oxygen of mass 25.0 g is confined in a vessel at 0°C and 1000. torr. Then 6.00 g of hydrogen is pumped into the vessel at constant temperature. What will be the final pressure in the vessel (assuming only mixing with no reaction)?
62. A gaseous mixture contains 3.23 g of chloroform, CHCl_3 , and 1.22 g of methane, CH_4 . Assuming that both compounds remain as gases, what pressure is exerted by the mixture inside a 50.0-mL metal container at 275°C? What pressure is contributed by the CHCl_3 ?
63. A cyclopropane-oxygen mixture can be used as an anesthetic. If the partial pressures of cyclopropane and oxygen are 140. torr and 560. torr, respectively, what is the ratio of the number of moles of cyclopropane to the number of moles of oxygen in this mixture? What is the corresponding ratio of molecules?
64. What is the mole fraction of each gas in a mixture having the partial pressures of 0.467 atm of He, 0.317 atm of Ar, and 0.277 atm of Xe?
65. Assume that unpolluted air has the composition shown in Table 12-2. (a) Calculate the number of molecules of N_2 , of O_2 , and of Ar in 1.00 L of air at 21°C and 1.00 atm. (b) Calculate the mole fractions of N_2 , O_2 , and Ar in the air.
66. Individual samples of O_2 , N_2 , and He are present in three 2.50-L vessels. Each exerts a pressure of 1.50 atm. (a) If

Molecular Weights and Formulas for Gaseous Compounds

53. Analysis of a volatile liquid shows that it contains 37.23% carbon, 7.81% hydrogen, and 54.96% chlorine by mass. At 150.°C and 1.00 atm, 500. mL of the vapor has a mass of 0.922 g. (a) What is the molecular weight (mass) of the compound? (b) What is its molecular formula?
54. A student was given a container of ethane, C_2H_6 , that had been closed at STP. By making appropriate measurements, the student found that the mass of the sample of ethane was 0.244 g and the volume of the container was 185 mL. Use the student's data to calculate the molecular weight (mass) of ethane. What percent error is obtained? Suggest some possible sources of the error.
55. Calculate the molecular weight (mass) of a gaseous element if 0.480 g of the gas occupies 367 mL at 365 torr and 45°C. Suggest the identity of the element.

- all three gases are forced into the same 1.00-L container with no change in temperature, what will be the resulting pressure? (b) What is the partial pressure of O_2 in the mixture? (c) What are the partial pressures of N_2 and He?
67. Hydrogen was collected over water at $20^\circ C$ and 757 torr. The volume of this gas sample was 35.3 mL. What volume would the dry hydrogen occupy at STP?



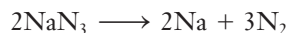
Charles D. Winters

H₂ collected over water

68. A nitrogen sample occupies 249 mL at STP. If the same sample were collected over water at $25^\circ C$ and 750. torr, what would be the volume of the gas sample?
69. ▲ A study of climbers who reached the summit of Mt. Everest without supplemental oxygen revealed that the partial pressures of O_2 and CO_2 in their lungs were 35 torr and 7.5 torr, respectively. The barometric pressure at the summit was 253 torr. Assume that the lung gases are saturated with moisture at a body temperature of $37^\circ C$. Calculate the partial pressure of inert gas (mostly nitrogen) in the climbers' lungs.
70. A 4.00-L flask containing He at 6.00 atm is connected to a 2.00-L flask containing N_2 at 3.00 atm and the gases are allowed to mix. (a) Find the partial pressures of each gas after they are allowed to mix. (b) Find the total pressure of the mixture. (c) What is the mole fraction of helium?
71. A 3.46-liter sample of a gas was collected over water on a day when the temperature was $21^\circ C$ and the barometric pressure was 718 torr. The dry sample of gas had a mass of 4.20 g. What is the molecular weight of the gas?

Stoichiometry in Reactions Involving Gases

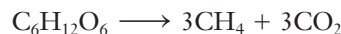
72. ● During a collision, automobile air bags are inflated by the N_2 gas formed by the explosive decomposition of sodium azide, NaN_3 .



What mass of sodium azide would be needed to inflate a 25.0-L bag to a pressure of 1.40 atm at $25^\circ C$?

73. Assuming the volumes of all gases in the reaction are measured at the same temperature and pressure, calculate the volume of water vapor obtainable by the explosive reaction of a mixture of 725 mL of hydrogen gas and 325 mL of oxygen gas.
74. ▲ One liter of sulfur vapor, $S_8(g)$, at $600^\circ C$ and 1.00 atm is burned in excess pure oxygen to give sulfur dioxide gas, SO_2 , measured at the same temperature and pressure. What mass of SO_2 gas is obtained?

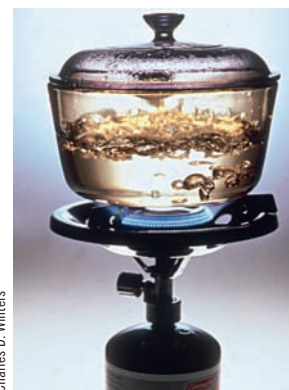
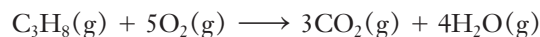
75. ● Calculate the volume of methane, CH_4 , measured at 300. K and 825 torr, that can be produced by the bacterial breakdown of 1.10 kg of a simple sugar.



76. ▲ A common laboratory preparation of oxygen is
- $$2KClO_3(s) \xrightarrow{\text{heat/MnO}_2} 2KCl(s) + 3O_2(g)$$

If you were designing an experiment to generate four bottles (each containing 250. mL) of O_2 at $25^\circ C$ and 762 torr and allowing for 25% waste, what mass of potassium chlorate would be required?

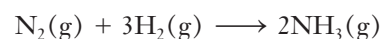
77. Many campers use small propane stoves to cook meals. What volume of air (see Table 12-2) will be required to burn 8.50 L of propane, C_3H_8 ? Assume all gas volumes are measured at the same temperature and pressure.



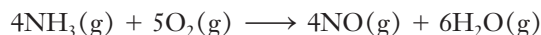
Charles D. Winters

Propane stove

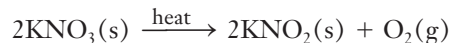
78. If 3.00 L of nitrogen and 7.00 L of hydrogen were allowed to react, how many liters of $NH_3(g)$ could form? Assume all gases are at the same temperature and pressure, and that the limiting reactant is used up.



79. We burn 12.50 L of ammonia in 20.00 L of oxygen at $500^\circ C$. What volume of nitric oxide, NO , gas can form? What volume of steam, $H_2O(g)$, is formed? Assume that all gases are at the same temperature and pressure, and that the limiting reactant is used up.



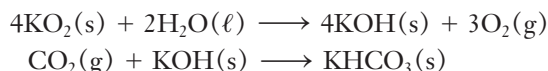
80. What mass of KNO_3 would have to be decomposed to produce 21.1 L of oxygen measured at STP?



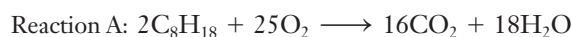
81. ● Refer to Exercise 80. An impure sample of KNO_3 that had a mass of 55.8 g was heated until all of the KNO_3 had decomposed. The liberated oxygen occupied 4.22 L at STP. What percentage of the sample was KNO_3 ? Assume that no impurities decompose to produce oxygen.



82. Heating a 5.913-g sample of an ore containing a metal sulfide, in the presence of excess oxygen, produces 1.177 L of dry SO₂, measured at 35.0°C and 755 torr. Calculate the percentage by mass of sulfur in the ore.
83. The following reactions occur in a gas mask (a self-contained breathing apparatus) sometimes used by underground miners. The H₂O and CO₂ come from exhaled air, and O₂ is inhaled as it is produced. KO₂ is potassium superoxide. The CO₂ is converted to the solid salt potassium hydrogen carbonate, KHCO₃, so that CO₂ is not inhaled in significant amounts.



- (a) What volume of O₂, measured at STP, is produced by the complete reaction of 1.25 g of KO₂? (b) What is this volume at body temperature, 37°C, and 1.00 atm? (c) What mass of KOH is produced in part (a)? (d) What volume of CO₂, measured at STP, will react with the mass of KOH of part (c)? (e) What is the volume of CO₂ in part (d) measured at 37°C and 1.00 atm?
84. Let us represent gasoline as octane, C₈H₁₈. When hydrocarbon fuels burn in the presence of sufficient oxygen, CO₂ is formed.



But when the supply of oxygen is limited, the poisonous gas carbon monoxide, CO, is formed.



Any automobile engine, no matter how well tuned, burns its fuel by some combination of these two reactions. Suppose an automobile engine is running at idle speed in a closed garage with air volume 97.5 m³. This engine burns 95.0% of its fuel by reaction A, and the remainder by reaction B. (a) How many liters of octane, density 0.702 g/mL, must be burned for the CO to reach a concentration of 2.00 g/m³? (b) If the engine running at idle speed burns fuel at the rate of 1.00 gal/h (0.0631 L/min), how long does it take to reach the CO concentration in (a)?

The Kinetic-Molecular Theory and Molecular Speeds

85. Outline the kinetic-molecular theory.
86. Place these gases in order of increasing average molecular speed at 25°C: Kr, CH₄, N₂, CH₂Cl₂.
87. How does the kinetic-molecular theory explain (a) Boyle's Law? (b) Dalton's Law? (c) Charles's Law?
88. SiH₄ molecules are heavier than CH₄ molecules; yet, according to kinetic-molecular theory, the average kinetic energies of the two gases at the same temperature are equal. How can this be?
89. At 22°C, Cl₂ molecules have some rms speed (which we need not calculate). At what temperature would the rms speed of F₂ molecules be the same?
90. (a) How do average speeds of gaseous molecules vary with temperature? (b) Calculate the ratio of the rms speed of N₂ molecules at 100.°C to the rms speed of the same molecules at 0.0°C.
91. How do the average kinetic energies and average speeds of each gas in a mixture compare?
92. (a) If you heat a gaseous sample in a fixed volume container, the pressure increases. Use the kinetic-molecular theory to explain the increased pressure. (b) If the volume of a gaseous sample is reduced at constant temperature, the pressure increases. Use the kinetic-molecular theory to explain the increase in pressure.

Deviations from Ideal Gas Behavior

93. What is the van der Waals equation? How does it differ from the ideal gas equation?
94. Which of the following gases would be expected to behave most nearly ideally under the same conditions: H₂, F₂, HF? Which one would be expected to deviate from ideal behavior the most? Explain both answers.
95. Does the effect of intermolecular attraction on the properties of a gas become more significant or less significant if (a) the gas is compressed to a smaller volume at constant temperature? (b) more gas is forced into the same volume at the same temperature? (c) the temperature of the gas is raised at constant pressure?
96. Does the effect of molecular volume on the properties of a gas become more significant or less significant if (a) the gas is compressed to a smaller volume at constant temperature? (b) more gas is forced into the same volume at the same temperature? (c) the temperature of the gas is raised at constant pressure?
97. In each pair of gases below, tell which will effuse faster: (a) CO₂ or F₂; (b) O₂ or N₂; (c) C₂H₄ or C₂H₆; (d) two chlorofluorocarbons: CFCl₃ or C₂Cl₂F₄.
98. Find the pressure of a sample of carbon tetrachloride, CCl₄, if 1.00 mol occupies 35.0 L at 77.0°C (slightly above its normal boiling point). Assume that CCl₄ obeys (a) the Ideal Gas Law; (b) the van der Waals equation. The van der Waals constants for CCl₄ are $a = 20.39 \text{ L}^2 \cdot \text{atm/mol}^2$ and $b = 0.1383 \text{ L/mol}$. (c) Repeat the calculations in parts (a) and (b) using a 3.10-mol gas sample confined to 5.75 L at 135°C.
99. A sample of gas has a molar volume of 10.1 L at a pressure of 745 torr and a temperature of -138°C. Is the gas behaving ideally?
100. You want to store 165 g of CO₂ gas in a 12.5-L tank at room temperature (25°C). Calculate the pressure the gas would have using (a) the Ideal Gas Law and (b) the van der Waals equation. For CO₂, $a = 3.59 \text{ atm} \cdot \text{L}^2/\text{mol}^2$ and $b = 0.0427 \text{ L/mol}$.
101. At higher temperatures and very low pressures, gases behave ideally, but as the pressure is increased the product PV becomes less than the product nRT . Give a molecular level explanation of this fact.

Mixed Exercises

102. Liquid iron at 1600.°C has a density of 6.88 g/cm³, and at 20.°C solid iron has a density of 7.86 g/cm³. Using these data, calculate the molar volume of iron at each temperature. Compare your calculated value with those in Table 12-1 for different compounds.
103. Given that the molar volume of liquid carbon dioxide at -37°C is 39.9 mL/mol and the molar volume of solid carbon dioxide at -79°C is 28.2 mL/mol, calculate the density of carbon dioxide at each set of conditions. If carbon dioxide were to act as an ideal gas, what would be its density at 50°C? When one compares each value for density to the state of the carbon dioxide, which phase change results in the greater change in density?
104. A student is to perform a laboratory experiment that requires the evolution and collection of 85 mL of dry oxygen gas at one atmosphere and 25°C. What is the minimum mass of water required to generate the oxygen by electrolysis of water?
105. A tilting McLeod gauge is used to measure very low pressures of gases in glass vacuum lines in the laboratory. It operates by compressing a large volume of gas at low pressure to a much smaller volume so that the pressure is more easily measured. What is the pressure of a gas in a vacuum line if a 53.3-mL volume of the gas, when compressed to 0.235 mL, supports a 16.9-mm column of mercury?



A McLeod gauge

106. Imagine that you live in a cabin with an interior volume of 175 m³. On a cold morning your indoor air temperature is 10.°C, but by the afternoon the sun has warmed the cabin air to 18°C. The cabin is not sealed; therefore, the pressure inside is the same as it is outdoors. Assume that the pressure remains constant during the day. How many cubic meters of air would have been forced out of the cabin by the sun's warming? How many liters?
107. A particular tank can safely hold gas up to a pressure of 44.3 atm. When the tank contains 38.1 g of N₂ at 25°C, the gas exerts a pressure of 10.1 atm. What is the highest temperature to which the gas sample can be heated safely?
108. Find the molecular weight (mass) of Freon-12 (a chlorofluorocarbon) if 8.29 L of vapor at 200.°C and 790. torr has a mass of 26.8 g.
109. Write an equation in which density is set equal to the terms R , P , T , and other terms, if needed.
110. Write an equation in which the relationship between P and T is expressed at constant n and V . Give a nonlaboratory example in which this relationship can be applied.
111. A flask of unknown volume was filled with air to a pressure of 3.25 atm. This flask was then attached to an evacuated flask with a known volume of 5.00 L, and the air was allowed to expand into the flask. The final pressure of the air (in both flasks) was 2.40 atm. Calculate the volume of the first flask.
112. Relative humidity is the ratio of the pressure of water vapor in the air to the pressure of water vapor in air that is saturated with water vapor at the same temperature.
- $$\text{relative humidity} = \frac{\text{actual partial pressure of H}_2\text{O}}{\text{partial pressure of H}_2\text{O vapor if sat'd}}$$
- Often this quantity is multiplied by 100 to give the percent relative humidity. Suppose the percent relative humidity is 80.0% at 91.4°F (33.0°C) in a house with volume 245 m³. Then an air conditioner is turned on. Due to the condensation of water vapor on the cold coils of the air conditioner, water vapor is also removed from the air as it cools. After the air temperature has reached 77.0°F (25.0°C), the percent relative humidity is measured to be 15.0%. (a) What mass of water has been removed from the air in the house? (*Reminder:* Take into account the difference in saturated water vapor pressure at the two temperatures.) (b) What volume would this liquid water occupy at 25°C? (Density of liquid water at 25.0°C = 0.997 g/cm³.)
113. A 450.-mL flask contains 0.500 g of nitrogen gas at a pressure of 744 torr. Are these data sufficient to allow you to calculate the temperature of the gas? If not, what is missing? If so, what is the temperature in °C?
114. Use both the Ideal Gas Law and the van der Waals equation to calculate the pressure exerted by a 4.00-mol sample of ammonia in a 25.0-L container at 100.°C. By what percentage of the ideal pressure do the two results differ?
115. What volume of hydrogen fluoride at 743 torr and 24°C will be formed by the reaction of 38.3 g of xenon difluoride with a stoichiometric amount of water? The *unbalanced* equation is
- $$\text{XeF}_2(\text{s}) + \text{H}_2\text{O}(\ell) \longrightarrow \text{Xe}(\text{g}) + \text{O}_2(\text{g}) + \text{HF}(\text{g})$$
- What volumes of oxygen and xenon will be formed under these conditions?
116. Cyanogen is 46.2% carbon and 53.8% nitrogen by mass. At a temperature of 25°C and a pressure of 750. torr, 1.00 g of cyanogen gas occupies 0.476 L. Determine the empirical formula and the molecular formula of cyanogen.
117. Incandescent light bulbs contain noble gases, such as argon, so that the filament will last longer. The approximate volume of a 100-watt bulb is 130. cm³, and the bulb contains 0.125 g of argon. How many grams of argon would be contained in a 150-watt bulb under the same pressure and temperature conditions if the volume of the larger wattage bulb were 180. cm³?



Molecular Reasoning exercises



More Challenging exercises

Blue-Numbered

exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

Conceptual Exercises

118. In the United Kingdom the Celsius scale has been used almost exclusively for expressing temperatures since the 1970s, except that some broadcasters and publications still quote Fahrenheit temperatures in weather forecasts for the benefit of those born before 1950. In London the average minimum temperature in December is 38. Is that more likely to be 38°F, 38°C, or 38 K? In July the average maximum temperature is 22. Is that more likely to be 22°F, 22°C, or 22 K? By contrast, in the permanently shaded south polar basin of the moon the surface temperature may be 40. Is that more likely to be 40°F, 40°C, or 40 K?
119. The effectiveness of a steam engine depends, in part, on the large change in volume that occurs when liquid water is converted to steam. The density of liquid water at 100°C is 0.958 g/mL and the density of steam at 100°C is 0.598 g/L. Calculate the molar volume of liquid water and steam at 100°C and the ratio of the molar volume of steam to that of liquid water.
120. ▲ An attempt was made to collect carbon dioxide, isolated from the decomposition of a carbonate-containing mineral, by first bubbling the gas through pure liquid acetic acid. The experiment yielded 500. mL of a gaseous mixture of acetic acid and carbon dioxide at 1.00 atm and 16.0°C. The vapor pressure of pure acetic acid at 16.0°C is 400. torr. What should be the total mass of the collected sample?
121. Acetylene (C_2H_2), the gas used in welders' torches, is produced by the reaction of calcium carbide (CaC_2) with water. The other reaction product is calcium hydroxide. (a) Write the chemical equation for the production of C_2H_2 . (b) What volume of C_2H_2 , measured at 22°C and 965 torr, would be produced from the complete reaction of 10.2 g of CaC_2 with 5.23 g of H_2O ?

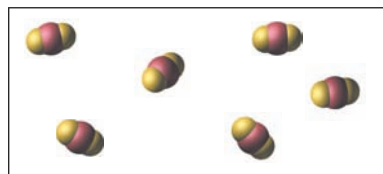


Charles D. Winters

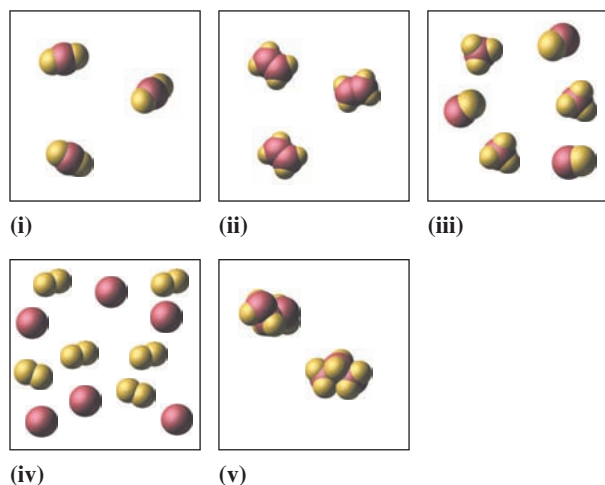
Acetylene torch

122. Redraw Figure 12-12 so that it not only depicts the decrease in space between molecules as the system is cooled from 600. K to 300. K but also emphasizes the change in kinetic energy.
123. Suppose you were asked to supply a particular mass of a specified gas in a container of fixed volume at a specified pressure and temperature. Is it likely that you could fulfill the request? Explain.

124. ●● The gas molecules in the box undergo a reaction at constant temperature and pressure.



- (a) If the initial volume is 2.5 L and the final volume is 1.25 L, which of the following boxes (i–v) could be the products of the reaction? Explain your reasoning.
 (b) Represent the pink atoms as “A” and the yellow atoms as “B,” and write the equation for the chemical reaction that occurs.



125. A 503-mL flask contains 0.0243 mol of an ideal gas at a given temperature and pressure. Another flask contains 0.0388 mol of the gas at the same temperature and pressure. What is the volume of the second flask?
126. Mole fraction is one of the few quantities that is expressed as a fraction. Frequently, percent is used instead. Cite an example earlier in this textbook where percent was used instead of a fraction. Write an equation that relates mole fraction and mole percent.
127. ●● Explain why gases at high pressure or low temperature are less likely to behave ideally.
128. Nitrogen, oxygen, argon, and carbon dioxide make up 99.997% (by volume) of air. However, a small amount of each of the other noble gases is present in air:

Gas	Partial Pressure, atm
Neon	0.00001818
Helium	0.00000524
Krypton	0.00000114
Xenon	0.000000087

How many atoms of xenon are there in each liter of air?

129. The octane rating of a gasoline is a measure of its autoignition (knock) resistance. It is a number that gives the percentage of isooctane (C_8H_{18}) in a mixture of isooctane and n-heptane (C_7H_{16}) that would have the same anti-knocking capacity. For example, “regular” gasoline, with an octane rating of 87, has the same tendency to knock as a mixture with 87% isooctane and 13% n-heptane. When isooctane combusts, it reacts with oxygen to produce carbon dioxide and water. Write the complete, balanced equation for the combustion of isooctane. One gallon of isooctane will produce 509 L of vapor at STP. When this gas burns, what volume of carbon dioxide, at STP, would be produced?
130. Because the average kinetic energies of molecules of different gases are equal at a given temperature, and the kinetic energy of a molecule is directly proportional to its mass and the square of its velocity, molecules of gases that have lower molecular weights have higher average velocities than molecules of gases that have higher molecular weights. At 25°C , does every molecule of hydrogen (H_2) have a higher velocity than every molecule of oxygen (O_2)? Would any molecules of hydrogen have velocities near 0 m/s? Would any molecules of oxygen have velocities greater than the average velocity of all the hydrogen molecules?
131. A gas that is “lighter than air” has a molecular weight less than the weighted average of the molecular weights of the gases in air, 28.966. So, how does a molecule like Freon-12 (CCl_2F_2), with a molecular weight of 120.9, get into the stratosphere?

Building Your Knowledge

132. A 5.00-L reaction vessel contains hydrogen at a partial pressure of 0.588 atm and oxygen gas at a partial pressure of 0.302 atm. Which element is the limiting reactant in the following reaction?
- $$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$
133. Suppose the gas mixture in Exercise 132 is ignited and the reaction produces the theoretical yield of the product. What would be the partial pressure of each substance present in the final mixture?
134. A sample of carbon was burned in pure oxygen, forming carbon dioxide. The CO_2 was then bubbled into 3.50 L of 0.437 M NaOH, forming sodium carbonate, as shown by the following reaction.



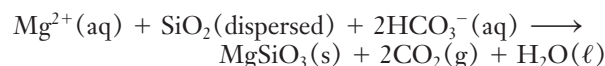
Following the reaction, the excess NaOH was exactly neutralized with 1.71 L of 0.350 M HCl. What volume of O_2 , measured at 8.6 atm and 20°C , was consumed in the process?

135. When magnesium carbonate, $MgCO_3$, is heated to a high temperature, it decomposes.



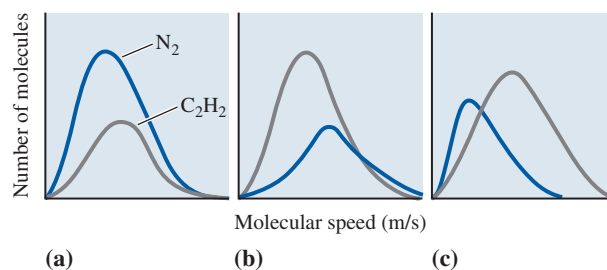
A 20.29-gram sample of impure magnesium carbonate is completely decomposed at 1000°C in a previously evacuated 2.00-L reaction vessel. After the reaction was complete, the solid residue (consisting only of MgO and the original impurities) had a mass of 15.90 grams. Assume that no other constituent of the sample produced a gas and that the volume of any solid was negligible compared with the gas volume. (a) How many grams of CO_2 were produced? (b) What was the pressure of the CO_2 produced? (c) What percent of the original sample was magnesium carbonate?

136. One natural source of atmospheric carbon dioxide is precipitation reactions such as the precipitation of silicates in the oceans.



How many grams of magnesium silicate would be precipitated during the formation of 100. L of carbon dioxide at 30°C and 775 torr?

137. Table 12-2 states that dry air is 20.94% (by volume) oxygen. What is the partial pressure of oxygen under the conditions of STP? *Hint:* For gaseous samples the mole ratios are equal to the volume ratios.
138. Sulfur dioxide is a common air pollutant. It is known to cause health problems, coughing, even death at concentrations of 1.4 mg/L of air. (a) What is the molarity of sulfur dioxide when its concentration is 0.135 mg/L? (b) What is the mole fraction of sulfur dioxide at a concentration of 1.4 mg/L? Assume that the density of dry air is 1.29 g/L.
139. Which graph represents the distribution of molecular speeds for the gases acetylene (C_2H_2) and N_2 ? Both gases are in the same container.



Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

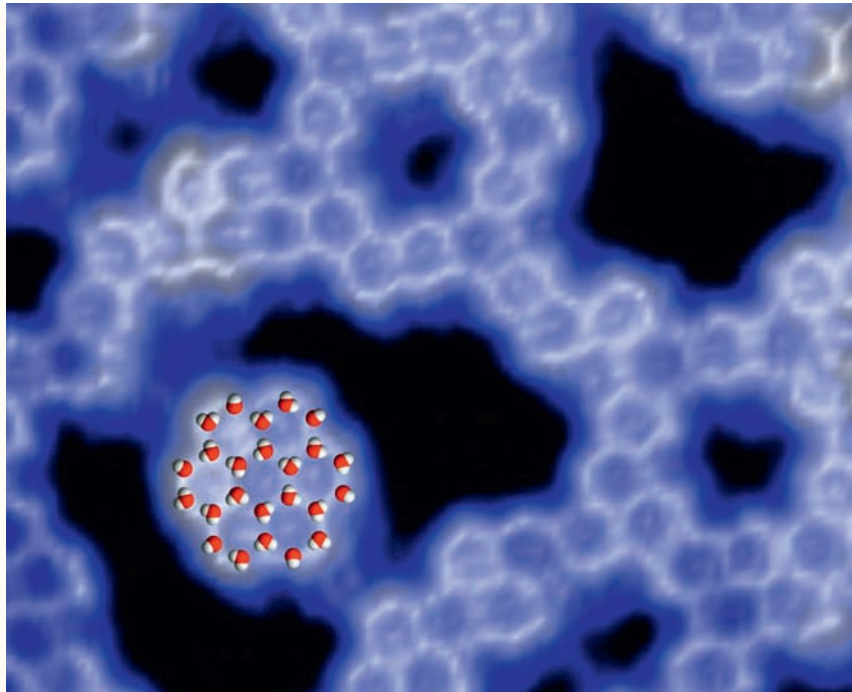
140. Go to www.liv.ac.uk/chemistry/links/refbiog.html and subsequent pages as needed or another website and locate information on gas laws as they relate to Boyle, Charles, and Dalton. (a) Did the careers of Boyle, Charles, and Dalton overlap? Which one's work is the most recent? (b) What physical impairment is also known as Daltonism? How is Daltonism related to John Dalton's death?



- 141.** Go to www.aquaholic.com/gasses/charles.htm and locate information on Charles's Law. (a) The relationship that "at constant volume, pressure divided by temperature is equal to a constant" was not given a name in this book by Whitten, Davis, Peck, and Stanley. In this website what is the name given to this relationship? What is wrong with this law as stated on this web page? (b) In the calculation of pressure, why was 14.7 subtracted from the calculated value of 3412.8?
- 142.** Go to www.liv.ac.uk/chemistry/links/refbiog.html or another website and locate information on the lives of Amedeo Avogadro, Stanislao Cannizzaro, and Jean Baptiste Dumas. (a) How were the careers of Amedeo Avogadro and Stanislao Cannizzaro intertwined? (b) How was Jean Baptiste Dumas associated with early studies of gases?

Liquids and Solids

13



Interfacial force microscopy (a form of scanning tunneling microscopy) gives an image of water wetting an extended surface of a metal such as palladium or ruthenium. Theoretical calculations based on these images give new clues for how water wets such surfaces. A proposed water rosette on the metal surface is represented as a space-filling model.

Courtesy of Professor Miquel Salmeron, Lawrence Berkeley National Laboratory

OUTLINE

13-1 Kinetic–Molecular Description of Liquids and Solids

13-2 Intermolecular Attractions and Phase Changes

The Liquid State

13-3 Viscosity

13-4 Surface Tension

13-5 Capillary Action

13-6 Evaporation

13-7 Vapor Pressure

13-8 Boiling Points and Distillation

13-9 Heat Transfer Involving Liquids

The Solid State

13-10 Melting Point

13-11 Heat Transfer Involving Solids

13-12 Sublimation and the Vapor Pressure of Solids

13-13 Phase Diagrams (P versus T)

13-14 Amorphous Solids and Crystalline Solids

13-15 Structures of Crystals

13-16 Bonding in Solids

13-17 Band Theory of Metals

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Describe the properties of liquids and solids and how they differ from gases
- ▶ Understand the kinetic–molecular description of liquids and solids, and show how this description differs from that for gases
- ▶ Use the terminology of phase changes
- ▶ Understand various kinds of intermolecular attractions and how they are related to physical properties such as vapor pressure, viscosity, melting point, and boiling point
- ▶ Describe evaporation, condensation, and boiling in molecular terms
- ▶ Calculate the heat transfer involved in warming or cooling without change of phase
- ▶ Calculate the heat transfer involved in phase changes
- ▶ Describe melting, solidification, sublimation, and deposition in molecular terms
- ▶ Interpret P versus T phase diagrams
- ▶ Describe the regular structure of crystalline solids
- ▶ Describe various types of solids
- ▶ Relate the properties of different types of solids to the bonding or interactions among particles in these solids
- ▶ Visualize some common simple arrangements of atoms in solids
- ▶ Carry out calculations relating atomic arrangement, density, unit cell size, and ionic or atomic radii in some simple crystalline arrangements
- ▶ Describe the bonding in metals
- ▶ Explain why some substances are conductors, some are insulators, and others are semiconductors

The molecules of most gases are so widely separated at ordinary temperatures and pressures that they do not interact with one another significantly. The physical properties of gases are reasonably well described by the simple relationships in Chapter 12. In liquids and solids, the so-called **condensed phases**, the particles are close together so they interact much more strongly. Although the properties of liquids and solids can be described, they cannot be adequately explained by simple mathematical relationships. Table 13-1 and Figure 13-1 summarize some of the characteristics of gases, liquids, and solids.

13-1 Kinetic–Molecular Description of Liquids and Solids

The properties listed in Table 13-1 can be qualitatively explained in terms of the kinetic–molecular theory of Chapter 12. We saw in Section 12-13 that the average kinetic energy of a collection of gas molecules decreases as the temperature is lowered. As a sample of gas is cooled and compressed, the rapid, random motion of gaseous molecules decreases. The molecules approach one another, and the intermolecular attractions increase. Eventually, these increasing intermolecular attractions overcome the reduced kinetic energies. At this point the gas changes to a liquid; this process is called condensation (liquefaction). The temperatures and pressures required for condensation vary from gas to gas, because different kinds of molecules have different attractive forces.

In the liquid state the forces of attraction among particles are great enough that disordered clustering occurs. The particles are so close together that very little of the volume occupied by a liquid is empty space. As a result, it is very hard to compress a liquid. Particles in liquids have sufficient energy of motion to overcome partially the attractive forces among them. They are able to slide past one another so that liquids assume the shapes of their containers up to the volume of the liquid.

Liquids diffuse into other liquids with which they are *miscible*. For example, when a drop of red food coloring is added to a glass of water, the water becomes red throughout after diffusion is complete. The natural diffusion rate is slow relative to gases at normal temperatures. Because the average separations among particles in liquids are far less than those in gases, the densities of liquids are much higher than the densities of gases (see Table 12-1).

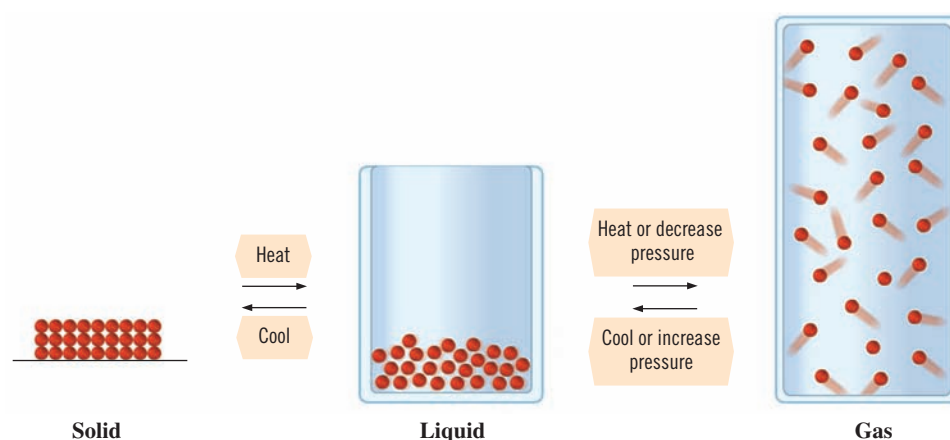
Cooling a liquid lowers its molecular kinetic energy, so its molecules slow down even more. If the temperature is lowered sufficiently, at ordinary pressures, stronger but shorter-range attractive interactions overcome the reduced kinetic energies of the

▶ Intermolecular attractions are those between different molecules or ions. Intramolecular attractions are those between atoms within a single molecule or ion.

▶ The *miscibility* of two liquids refers to their ability to mix and produce a homogeneous solution.

Table 13-1 Some Characteristics of Solids, Liquids, and Gases

Solids	Liquids	Gases
1. Have definite shape (resist deformation) 2. Are nearly incompressible 3. Usually have higher density than liquids 4. Are not fluid 5. Diffuse only very slowly through solids 6. Have an ordered arrangement of particles that are very close together; particles usually have only vibrational motion	1. Have no definite shape (assume shapes of containers) 2. Have definite volume (are only very slightly compressible) 3. Have high density 4. Are fluid 5. Diffuse through other liquids 6. Consist of disordered clusters of particles that are quite close together; particles have random motion in three dimensions	1. Have no definite shape (fill containers completely) 2. Are compressible 3. Have low density 4. Are fluid 5. Diffuse rapidly 6. Consist of extremely disordered particles with much empty space between them; particles have rapid, random motion in three dimensions

**Figure 13-1** Representations of the kinetic-molecular description of the three phases of matter.

molecules to cause *solidification*. The temperature required for *crystallization* at a given pressure depends on the nature of short-range interactions among the particles and is characteristic of each substance.

Most solids have ordered arrangements of particles with a very restricted range of motion. Particles in the solid state cannot move freely past one another so they only vibrate about fixed positions. Consequently, solids have definite shapes and volumes. Because the particles are so close together, solids are nearly incompressible and are very dense relative to gases. Solid particles do not diffuse readily into other solids. However, analysis of two blocks of different solids, such as copper and lead, that have been pressed together for a period of years shows that each block contains some atoms of the other element. This demonstrates that solids do diffuse, but very slowly (Figure 13-2).

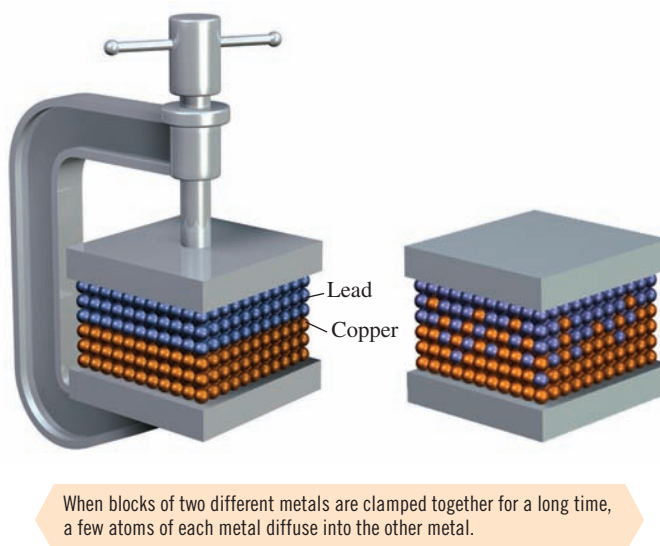
► **Solidification and crystallization** refer to the process in which a liquid changes to a solid. Crystallization is the more specific term, referring to the formation of a very ordered solid material.

13-2 Intermolecular Attractions and Phase Changes

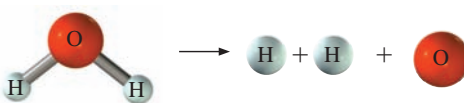
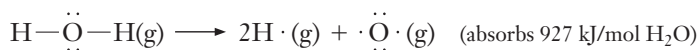
We have seen (see Section 12-15) how the presence of strong attractive forces between gas molecules can cause gas behavior to become nonideal when the molecules get close together at higher pressures. In liquids and solids the molecules are much closer together than in gases. As a result, properties of liquids, such as boiling point, vapor pressure, viscosity, and heat of vaporization, depend markedly on the strengths of the intermolecular attractive forces. These forces are also directly related to the properties of solids, such as melting point and heat of fusion. As the basis for our study of these condensed phases, let us discuss the types of attractive forces that can exist between molecules and ions.

Unless otherwise noted, all content on this page is © Cengage Learning.

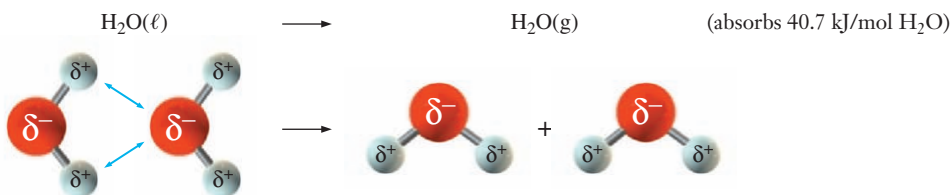
Figure 13-2 A representation of diffusion in solids.



Intermolecular forces refer to the forces *between* individual particles (atoms, molecules, ions) of a substance. These forces are quite weak relative to **intramolecular forces**, that is, covalent and ionic bonds *within* compounds. For example, 927 kJ of energy is required to decompose one mole of water vapor into H and O atoms. This reflects the strength of intramolecular forces (covalent bonds).



Only 40.7 kJ is required to convert one mole of liquid water into steam at 100°C.



STOP & THINK

It is important to be able to tell whether a substance is ionic, nonpolar covalent, or polar covalent. You should review the discussion of bonding in Chapters 7 and 8.

This reflects the lower strength of the intermolecular forces of attraction between the water molecules, compared to the covalent bonds within the water molecules. The attractive forces between water molecules are mainly due to *hydrogen bonding*.

If it were not for the existence of intermolecular attractions, condensed phases (liquids and solids) could not exist. These are the forces that hold the particles close to one another in liquids and solids. As we shall see, the effects of these attractions on melting points of solids parallel those on boiling points of liquids. High boiling and melting points are associated with substances that have strong intermolecular attractions. Let us consider the effects of the general types of forces that exist among ionic, covalent, and monatomic species.

Ion–Ion Interactions

According to Coulomb's Law, the *force of attraction* between two oppositely charged ions is directly proportional to the charges on the ions, q^+ and q^- , and inversely proportional to the square of the distance between them, d .

$$F \propto \frac{q^+ q^-}{d^2}$$

Energy has the units of force $\times$ distance, $F \times d$, so the *energy of attraction* between two oppositely charged ions is directly proportional to the charges on the ions and inversely proportional to the distance of separation.

$$E \propto \frac{q^+ q^-}{d}$$

Ionic compounds such as NaCl, CaBr₂, and K₂SO₄ exist as extended arrays of discrete ions in the solid state. As we shall see in Section 13-16, the oppositely charged ions in these arrays are quite close together. As a result of these small distances, d , the energies of attraction in these solids are substantial. Most ionic bonding is strong, and as a result most ionic compounds have relatively high melting points (Table 13-2). At high enough temperatures, ionic solids melt as the added heat energy overcomes the potential energy associated with the attraction of oppositely charged ions. The ions in the resulting liquid samples are free to move about, which accounts for the excellent electrical conductivity of molten ionic compounds.

For most substances, the liquid is less dense than the solid. Melting a solid nearly always produces greater average separations among the particles. This means that the forces (and energies) of attractions among the ions in an ionic liquid are less than in the solid state because the average d is greater in the melt. However, these energies of attraction are still much greater in magnitude than the energies of attraction among neutral species (molecules or atoms).

The product $q^+ q^-$ increases as the charges on ions increase. Ionic substances containing multiply charged ions, such as Al³⁺, Mg²⁺, O²⁻, and S²⁻ ions, *usually* have higher melting and boiling points than ionic compounds containing only singly charged ions, such as Na⁺, K⁺, F⁻, and Cl⁻. For a series of ions of similar charges, the closer approach of smaller ions results in stronger interionic attractive forces and higher melting points (compare NaF, NaCl, and NaBr in Table 13-2).

► When oppositely charged ions are close together, d (the denominator) is small, so F , the attractive force between them, is large.

► The covalent bonding *within* a polyatomic ion such as NH₄⁺ or SO₄²⁻ is very strong, but the forces that hold the *entire substance* together are ionic. Thus a compound that contains a polyatomic ion is an ionic compound (see Section 7-12).

STOP & THINK

The simple concepts of ion size and magnitudes of the ionic charges combined with Coulomb's Law can give you very good guidance on understanding a number of solid-state properties ranging from melting point trends to solubility.

Dipole–Dipole Interactions

Permanent dipole–dipole interactions occur between polar covalent molecules because of the attraction of the δ^+ atoms of one molecule to the δ^- atoms of another molecule (see Section 7-11).

Electrostatic forces between two ions decrease by the factor $1/d^2$ as their separation distance, d , increases. But dipole–dipole forces vary as $1/d^4$. Because of the higher power of d in the denominator, $1/d^4$ diminishes with increasing d much more rapidly than does

Table 13-2 Melting Points of Some Ionic Compounds

Compound	mp (°C)	Compound	mp (°C)	Compound	mp (°C)
NaF	993	CaF ₂	1423	MgO	2800
NaCl	801	Na ₂ S	1180	CaO	2580
NaBr	747	K ₂ S	840	BaO	1923
KCl	770				

Unless otherwise noted, all content on this page is © Cengage Learning.

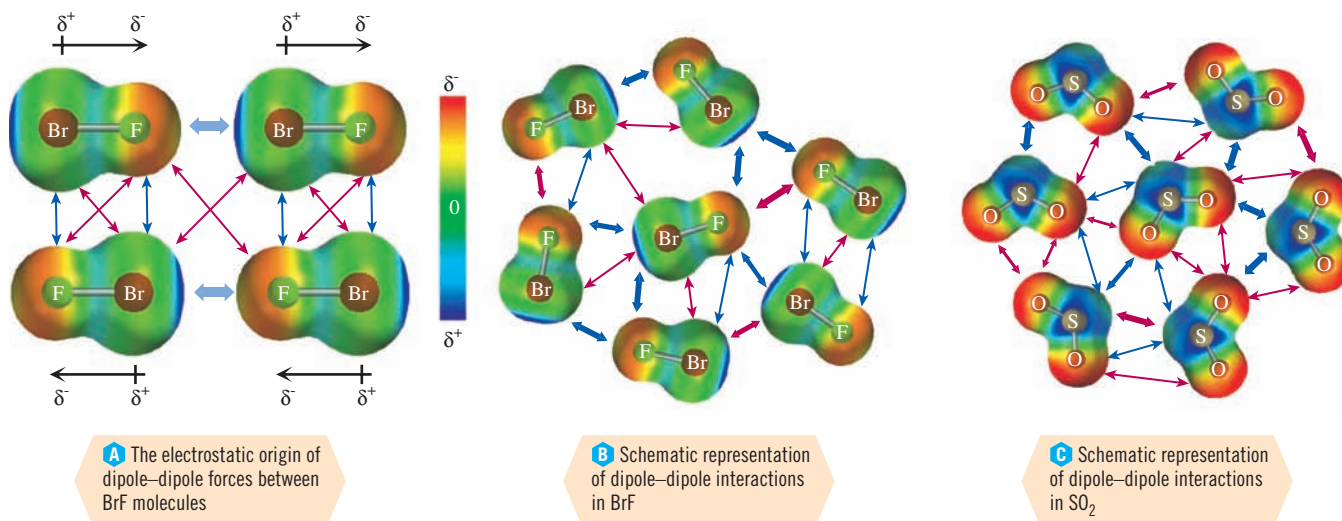


Figure 13-3 Dipole-dipole interactions among polar molecules. Each polar molecule is shaded with regions of highest negative charge (δ^-) in red and regions of highest positive charge (δ^+) colored blue. Attractive forces are shown as blue arrows, and repulsive forces are shown as red arrows. Stronger attractions and repulsions are indicated by thicker arrows. Molecules tend to arrange themselves to maximize attractions by bringing regions of opposite charge together while minimizing repulsions by separating regions of like charge.

$1/d^2$. As a result, dipole forces are effective only over very short distances. Furthermore, for dipole-dipole forces, q^+ and q^- represent only “partial charges,” so these forces are weaker than ion-ion forces. Average dipole-dipole interaction energies are approximately 4 kJ per mole of bonds. They are much weaker than ionic and covalent bonds, which have typical energies of about 400 kJ per mole of bonds. Substances in which permanent dipole-dipole interactions affect physical properties include bromine fluoride, BrF, and sulfur dioxide, SO₂. Dipole-dipole interactions are illustrated in Figure 13-3. All dipole-dipole interactions, including hydrogen bonding (discussed in the following section), are somewhat directional. An increase in temperature causes an increase in translational, rotational, and vibrational motion of molecules. This produces more random orientations of molecules relative to one another. Consequently, dipole-dipole interactions become less important as temperature increases. All these factors make compounds having only dipole-dipole interactions more volatile than ionic compounds.

Hydrogen Bonding

Hydrogen bonds are a special case of strong dipole-dipole interaction. They are not really chemical bonds in the formal sense.

Strong hydrogen bonding occurs among polar covalent molecules containing H bonded to one of the three small, highly electronegative elements—F, O, or N.

Like ordinary dipole-dipole interactions, hydrogen bonds result from the electrostatic attractions between δ^+ atoms of one molecule, in this case H atoms, and the δ^- atoms of another molecule. The small sizes of the F, O, and N atoms, combined with their high electronegativities, concentrate the electrons of these molecules around these δ^- atoms. This causes an H atom bonded to one of these highly electronegative elements to become quite positive. The δ^+ H atom is attracted to a lone pair of electrons on an F, O, or N atom other than the atom to which it is covalently bonded (Figure 13-4). The molecule that contains the hydrogen-bonding δ^+ H atom is often referred to as the *hydrogen-bond donor*; the δ^- atom to which it is attracted is called the *hydrogen-bond acceptor*.

Recently, careful studies of light absorption and magnetic properties in solution and of the arrangements of molecules in solids have led to the conclusion that the same kind of attraction occurs (although more weakly) when H is bonded to carbon. In some cases, very weak $\text{C}-\text{H} \cdots \text{O}$ “hydrogen bonds” exist. Similar observations suggest the existence of weak hydrogen bonds to chlorine atoms, such as $\text{O}-\text{H} \cdots \text{Cl}$. However, most chemists usually restrict usage of the term “hydrogen bonding” to compounds in which H is covalently bonded to F, O, or N, and we will do likewise throughout this text.

Typical hydrogen-bond energies are in the range 15 to 20 kJ/mol, which is four to five times greater than the energies of other dipole–dipole interactions. As a result, hydrogen bonds exert a considerable influence on the properties of substances. Hydrogen bonding is responsible for the unusually high melting and boiling points of compounds such as water, methyl alcohol, and ammonia (see Figure 13-4) compared with other compounds of similar molecular weight and molecular geometry (Figure 13-5). Hydrogen bonding between amino acid subunits, for example, is very important in establishing the three-dimensional structures of proteins.

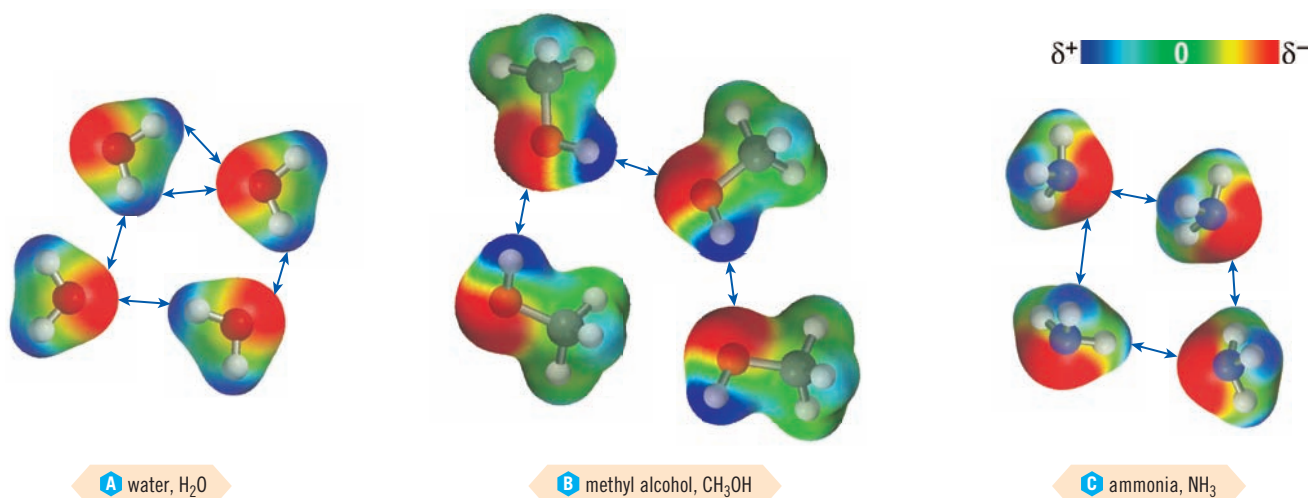


Figure 13-4 Hydrogen bonding (indicated by blue arrows) in (a) water, H_2O ; (b) methyl alcohol, CH_3OH ; and (c) ammonia, NH_3 . Hydrogen bonding is a special case of very strong dipole interaction. The hydrogen bonding is due to the electrostatic attraction of the δ^+ charged hydrogen of one molecule and the δ^- charged oxygen or nitrogen atom of another.

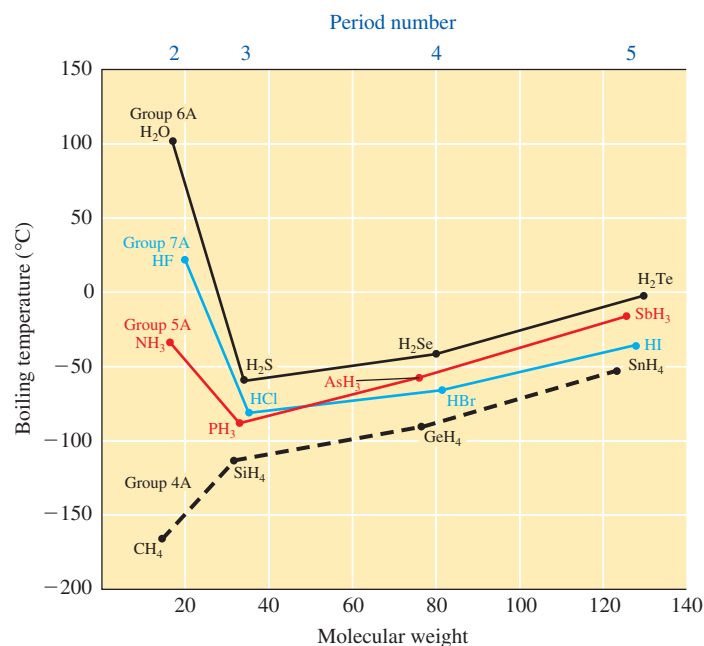


Figure 13-5 Boiling points of some hydrides as a function of molecular weight. The unusually high boiling points of NH_3 , H_2O , and HF compared with those of other hydrides of the same groups are due to hydrogen bonding. The electronegativity difference between H and C is small, and there are no unshared pairs on C; thus, CH_4 is not hydrogen bonded. Increasing molecular weight corresponds to increasing number of electrons; this makes the electron clouds easier to deform and causes increased dispersion forces, accounting for the increase in boiling points for the nonhydrogen-bonded members of each series.

Unless otherwise noted, all content on this page is © Cengage Learning.

Dispersion Forces

► Dispersion forces are often called **London forces**, after the German-born physicist Fritz London (1900–1954). He initially postulated their existence in 1930, on the basis of quantum theory. Yet another name is **van der Waals** attractive forces. You should be familiar with all three names.

Dispersion forces are weak attractive forces that are important only over *extremely* short distances because they vary as $1/d^7$. These forces are present between all types of molecules in condensed phases but are weak for small molecules. Dispersion forces are the only kind of intermolecular forces present among symmetrical nonpolar substances such as SO_3 , CO_2 , O_2 , N_2 , Br_2 , H_2 , and monatomic species such as the noble gases. Without dispersion forces, such substances could not condense to form liquids or solidify to form solids. Condensation of some substances occurs only at very low temperatures and/or high pressures.

Dispersion forces result from the attraction of the positively charged nucleus of one atom for the electron cloud of an atom in nearby molecules. This induces *temporary* dipoles in neighboring atoms or molecules. As electron clouds become larger and more diffuse, they are attracted less strongly by their own (positively charged) nuclei. Thus, they are more easily distorted, or *polarized*, by adjacent atoms or molecules. Dispersion forces are depicted in Figure 13-6. They exist in all substances.

Polarizability increases with increasing numbers of electrons and therefore with increasing sizes of molecules. Therefore, dispersion forces are generally stronger for molecules that are larger or that have more electrons. For molecules that are large or quite polarizable the total effect of dispersion forces can be even higher than dipole–dipole interactions or hydrogen bonding.



For a physical analogy to dispersion forces think about Velcro. Each little hook and loop in Velcro represents a very weak interaction. But adding them all together can make the total attraction very strong.

Figure 13-5 shows that polar covalent compounds with hydrogen bonding (H_2O , HF , NH_3) boil at higher temperatures than analogous polar compounds without hydrogen bonding (H_2S , HCl , PH_3). Symmetrical, nonpolar compounds (CH_4 , SiH_4) of comparable molecular weight boil at lower temperatures. In the absence of hydrogen bonding, boiling points of analogous substances (CH_4 , SiH_4 , GeH_4 , SnH_4) increase fairly regularly with increasing number of electrons and molecular size (molecular weight). This is due to

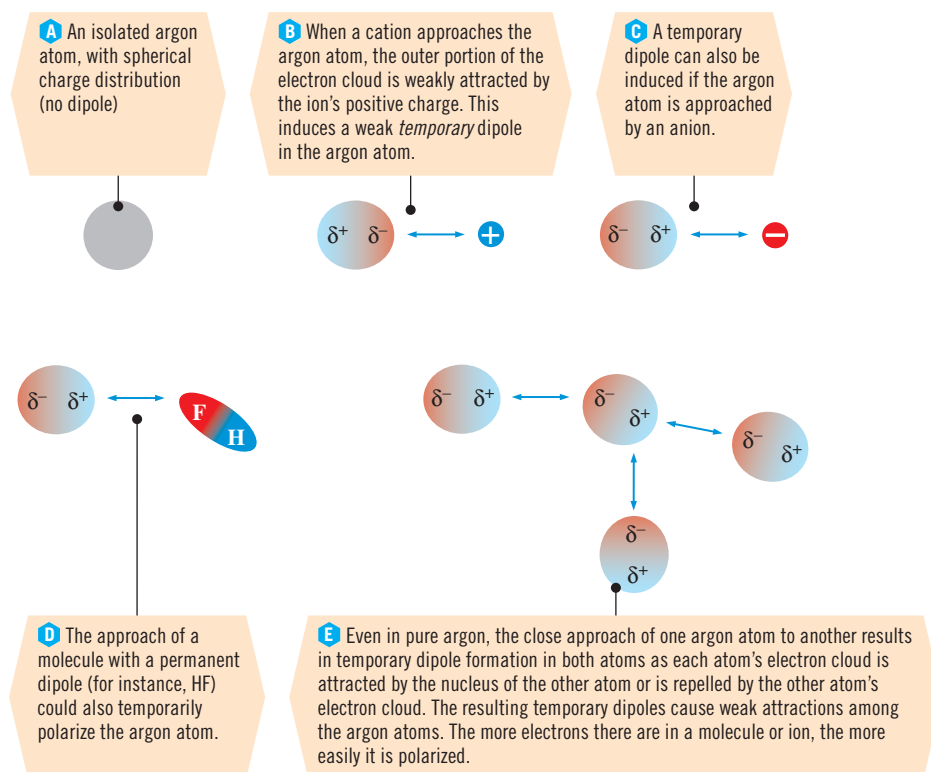


Figure 13-6 An illustration of how a temporary dipole can be induced in an atom.

increasing effectiveness of dispersion forces of attraction in the larger molecules and occurs even in the case of some polar covalent molecules. The increasing effectiveness of dispersion forces, for example, accounts for the increase in boiling points in the sequences $\text{HCl} < \text{HBr} < \text{HI}$ and $\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$, which involve nonhydrogen-bonded polar covalent molecules. The differences in electronegativities between hydrogen and other nonmetals *decrease* in these sequences, and the increasing dispersion forces override the decreasing permanent dipole–dipole forces. The *permanent* dipole–dipole interactions therefore have very little effect on the boiling point trend of these compounds.

Let's compare the magnitudes of the various contributions to the total energy of interactions in some simple molecules. Table 13-3 shows the permanent dipole moments and the energy contributions for five simple molecules. The contribution from dispersion forces is substantial in all cases. The permanent dipole–dipole energy is greatest for substances in which hydrogen bonding occurs. The variations of these total energies of interaction are closely related to molar heats of vaporization. As we shall see in Section 13-9, the heat of vaporization measures the amount of energy required to overcome the attractive forces that hold the molecules together in a liquid.

The properties of a liquid or a solid are often the result of many forces. The properties of an ionic compound are determined mainly by the very strong ion–ion interactions, even though other forces may also be present. In a polar covalent compound that contains $\text{N} - \text{H}$, $\text{O} - \text{H}$, or $\text{F} - \text{H}$ bonds, strong hydrogen bonding is often the strongest force present. If hydrogen bonding is absent in a polar covalent compound, dipole–dipole forces are likely to be the most important. In a slightly polar or nonpolar covalent compound or a monatomic nonmetal, the dispersion forces, though weak, are the strongest ones present, so they determine the overall attraction between molecules. For large molecules, even the very weak dispersion forces can total up to a considerable interactive force.

Table 13-3 Approximate Contributions to the Total Energy of Interaction Between Molecules, in kJ/mol

Molecule	Permanent Dipole Moment (D)	Permanent Dipole–Dipole Energy	Dispersion Energy	Total Energy	Molar Heat of Vaporization (kJ/mol)
Ar	0	0	8.5	8.5	6.7
CO	0.1	≈ 0	8.7	8.7	8.0
HCl	1.03	3.3*	17.8	21	16.2
NH_3	1.47	13*	16.3	29	27.4
H_2O	1.85	36*	10.9	47	40.7

*Hydrogen-bonded.

© Minden Pictures/SuperStock



The ability of the Tokay gecko to climb on walls and ceilings is due to the dispersion forces between the tiny hairs on the gecko's foot and the surface.

EXAMPLE 13-1 Intermolecular Forces

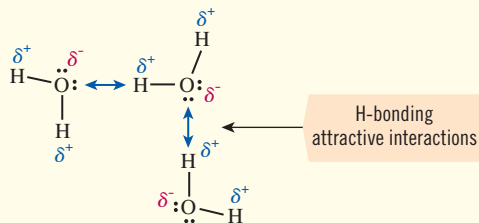
Identify the types of intermolecular forces that are present in a condensed phase (liquid or solid) sample of each of the following. For each, make a sketch, including a few molecules, that represents the major type of force: (a) water, H_2O ; (b) iodine, I_2 ; (c) nitrogen dioxide, NO_2 .

Plan

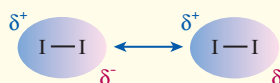
Any substance exhibits dispersion forces, which are generally weaker than other forces that might be present. To identify other possible forces, we must determine whether the molecule is polar (which can lead to dipole–dipole forces) or whether it can form hydrogen bonds.

Solution

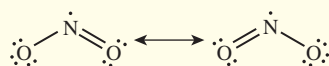
- (a) Water, H_2O , is polar, with the H sufficiently positive and the O sufficiently negative to form strong hydrogen bonds in addition to the dispersion forces that are present for any condensed phase. Hydrogen bonds are the strongest intermolecular forces present in this liquid.



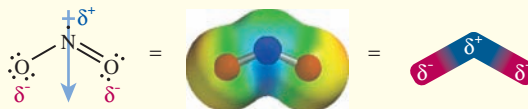
- (b) Iodine, I_2 , is nonpolar. The close approach of two I_2 molecules easily distorts the large electron cloud of each molecule, causing **dispersion forces** resulting in a temporary weak attraction. Because the molecule is nonpolar, other stronger forces are absent.



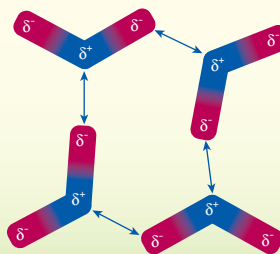
- (c) The Lewis formula of nitrogen dioxide, NO_2 , is shown by the following two resonance formulas:



This molecule contains N—O polar bonds, and the VSEPR approach (see Chapter 8) lets us conclude that the molecule is angular. It is therefore a polar molecule, which we can represent as



The positive part of one molecule is attracted to the negative parts of its neighbors, so there are **dipole–dipole interactions** in addition to the usual **dispersion forces**. Dipole–dipole attractions are the strongest ones between these molecules and can be represented as



You should now work Exercise 124.

STOP & THINK

Many properties of liquids and solids depend on intermolecular attractions. You must learn to use the electronic structure of a molecule or ion to predict which types of intermolecular forces it can exhibit.

The Liquid State

We shall briefly describe several properties of the liquid state. These properties vary markedly among various liquids, depending on the nature and strength of the attractive forces among the particles (atoms, molecules, ions) making up the liquid.

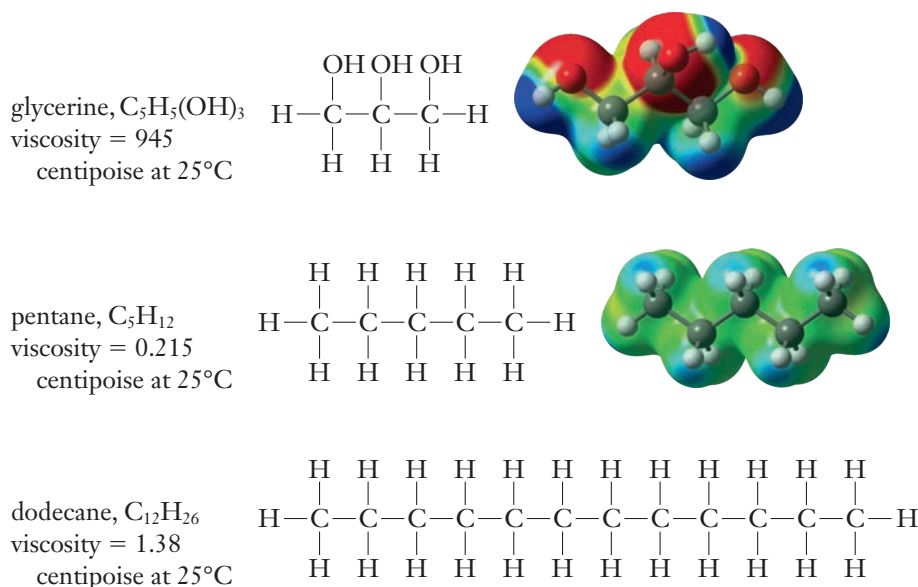
13-3 Viscosity

Viscosity is the resistance to flow of a liquid. Honey, which flows very slowly at room temperature, has a high viscosity while gasoline has a low viscosity. The viscosity of a liquid can be measured with a viscometer such as the one in Figure 13-7.

For a liquid to flow, the molecules must be able to slide past one another. In general, the stronger the intermolecular forces of attraction, the more viscous the liquid is. Substances that have a great ability to form hydrogen bonds, especially involving several hydrogen-bonding sites per molecule, such as glycerine (see structure below), usually have high viscosities. Increasing the size and surface area of molecules generally results in increased viscosity, due to the increased dispersion forces. For example, the shorter-chain hydrocarbon pentane (a free-flowing liquid at room temperature) is less viscous than dodecane (an oily liquid at room temperature). The longer the molecules are, the more they attract one another via dispersion forces, and the harder it is for them to flow.

► The *poise* is the unit used to express viscosity. The viscosity of water at 25°C is 0.89 centipoise.

► The “weight” of motor oil actually refers to its viscosity. SAE 40 oil (“40-weight”) is more viscous than SAE 10 oil.



► $\left(\begin{array}{c} \text{stronger} \\ \text{attractive} \\ \text{forces} \end{array} \right) \longleftrightarrow \left(\begin{array}{c} \text{higher} \\ \text{viscosity} \end{array} \right)$
 $\left(\begin{array}{c} \text{increasing} \\ \text{temperature} \end{array} \right) \longleftrightarrow \left(\begin{array}{c} \text{lower} \\ \text{viscosity} \end{array} \right)$

As temperature increases and the molecules move more rapidly, their kinetic energies are better able to overcome intermolecular attractions. Thus, viscosity decreases with increasing temperature, as long as no changes in composition occur.



Honey is a very viscous liquid.

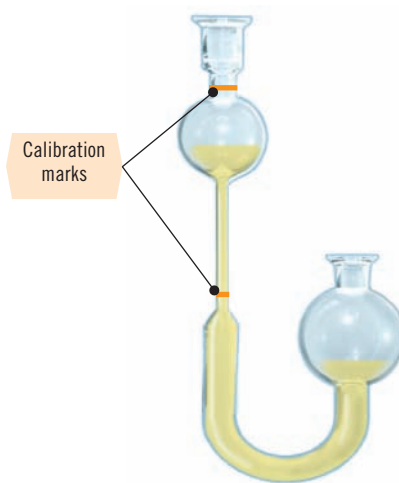


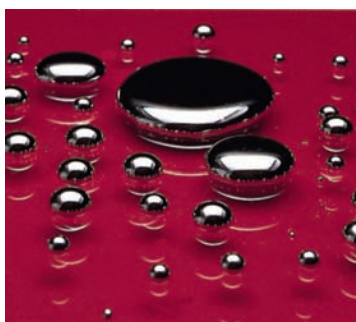
Figure 13-7 The Ostwald viscometer, a device used to measure viscosity of liquids. The time it takes for a known volume of a liquid to flow through a narrow neck of known size is measured. Liquids with low viscosities flow rapidly.



The surface tension of water supports this water strider. The nonpolar surfaces of its feet also help to repel the water.

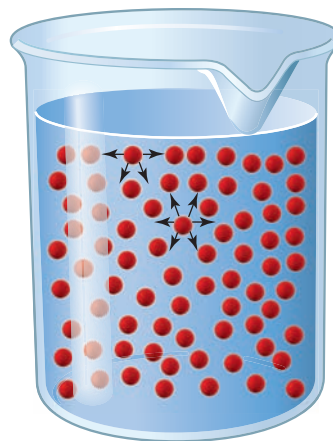


The shape of a soap bubble is due to the inward force (surface tension) that acts to minimize the surface area.



Droplets of mercury lying on a glass surface. The small droplets are almost spherical, whereas the larger droplets are flattened due to the effects of gravity. This shows that surface tension has more influence on the shape of the small (lighter) droplets.

Figure 13-8 A molecular-level view of the attractive forces experienced by molecules at and below the surface of a liquid.



13-4 Surface Tension

Molecules below the surface of a liquid are influenced by intermolecular attractions from all directions. Those on the surface, however, are attracted only toward the interior (Figure 13-8); these attractions pull the surface layer toward the center. The most stable situation is one in which the surface area is minimal. For a given volume, a sphere has the least possible surface area, so drops of liquid tend to assume spherical shapes. **Surface tension** is a measure of the inward forces that must be overcome to expand the surface area of a liquid.

13-5 Capillary Action

All forces holding a liquid together are called **cohesive forces**. The forces of attraction between a liquid and another surface are **adhesive forces**. The partial positive charges on the H atoms of water hydrogen bond strongly to the partial negative charges on the oxygen atoms at the surface of the glass. As a result, water *adheres* to glass, or is said to *wet* glass. As water creeps up the side of the glass tube, its favorable area of contact with the glass increases. The surface of the water, its **meniscus**, has a concave shape (Figure 13-9). On the other hand, mercury does not wet glass because its cohesive forces are much stronger than its attraction to glass. Thus, its meniscus is convex. **Capillary action** occurs when one end of a capillary tube, a glass tube with a small bore (inside diameter), is immersed in a liquid. If adhesive forces exceed cohesive forces, the liquid creeps up the sides of the tube until a balance is reached between adhesive forces and the weight of liquid. The smaller the bore, the higher the liquid climbs. Capillary action helps plant roots take up water and dissolved nutrients from the soil and transmit them up the stems. The roots, like glass, exhibit strong adhesive forces for water. Osmotic pressure (see Section 14-15) also plays a major role in this process.



Coating glass with a silicone polymer greatly reduces the adhesion of water to the glass. The left side of each glass has been treated with Rain-X®, which contains a silicone polymer. Water on the treated side forms droplets that are easily swept away.



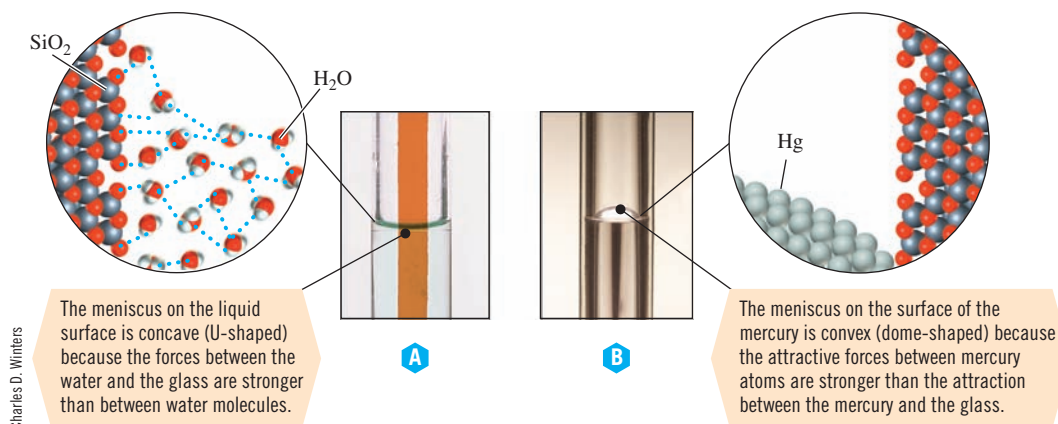


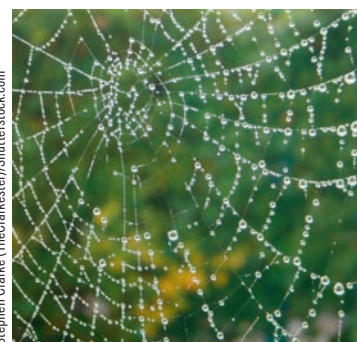
Figure 13-9 The meniscus, as observed in glass tubes (a) with water (concave) and (b) with mercury (convex).

13-6 Evaporation

Evaporation, or **vaporization**, is the process by which molecules on the surface of a liquid break away and go into the gas phase (Figure 13-10). Kinetic energies of molecules in liquids depend on temperature in the same way as they do in gases. The distribution of kinetic energies among liquid molecules at two different temperatures is shown in Figure 13-11. To break away from the attractions of its neighbors, a molecule must possess at least some minimum kinetic energy. Figure 13-11 shows that at a higher temperature, a greater fraction of molecules possess at least that minimum energy. The rate of evaporation increases as temperature increases.

Only the higher-energy molecules can escape from the liquid phase. The average molecular kinetic energy of the molecules remaining in the liquid state is thereby lowered, resulting in a lower temperature in the liquid. The liquid would then be cooler than its surroundings, so it absorbs heat from its surroundings. The cooling of your body by evaporation of perspiration is a familiar example of the cooling of the surroundings by evaporation of a liquid. This is called “cooling by evaporation.”

A molecule in the vapor may strike the liquid surface and be captured there. This process, the reverse of evaporation, is called **condensation**. As evaporation occurs in a closed container, the volume of liquid decreases and the number of gas molecules above the surface increases. Because more gas phase molecules can then collide with the surface, the rate of condensation increases. The system composed of the liquid and gas molecules of



The dew on this spider web was formed by condensation of water vapor from the air.

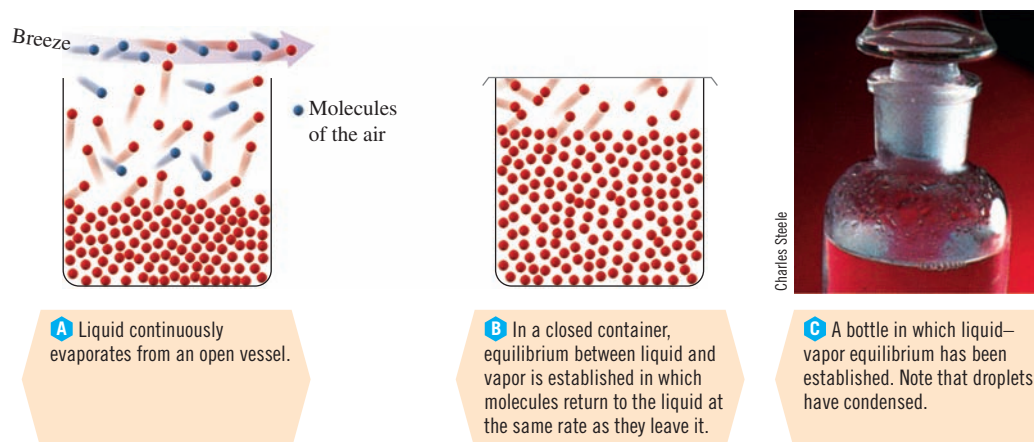


Figure 13-10

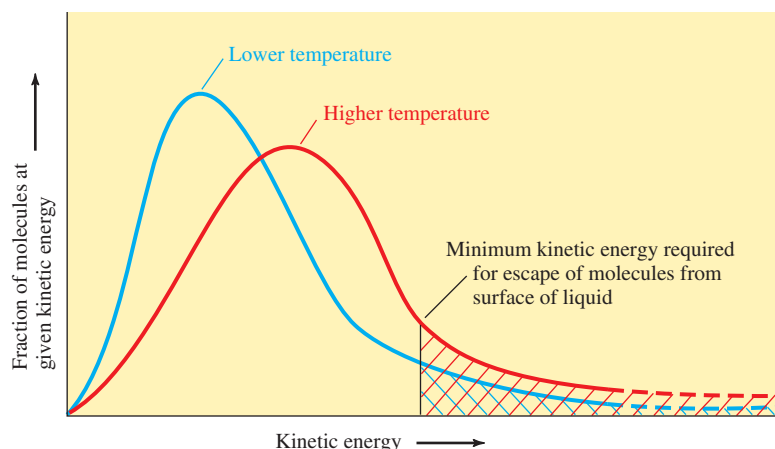
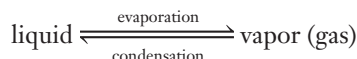


Figure 13-11 Distribution of kinetic energies of molecules in a liquid at different temperatures. At the lower temperature, a smaller fraction of the molecules have the energy required to escape from the liquid, so evaporation is slower and the equilibrium vapor pressure (Section 13-7) is lower.

► As an analogy, suppose that 30 students per minute leave a classroom, moving into the closed hallway outside, and 30 students per minute enter it. The total number of students in the room would remain constant, as would the total number of students in the hallway.

the same substance eventually achieves a **dynamic equilibrium** in which the rate of evaporation equals the rate of condensation in the closed container.



The two opposing rates are not zero, but are equal to one another—hence we call this “dynamic,” rather than “static,” equilibrium. Even though evaporation and condensation are both continuously occurring, *no net change occurs* because the rates are equal.

If the vessel were left open to the air, however, this equilibrium could not be reached. Molecules would diffuse away, and slight air currents would also sweep some gas molecules away from the liquid surface. This would allow more evaporation to occur to replace the lost vapor molecules. Consequently, a liquid can eventually evaporate entirely if it is left uncovered. This situation illustrates **LeChatelier’s Principle**:

A system at equilibrium, or changing toward equilibrium, responds in the way that tends to relieve or “undo” any stress placed on it.

In this example the stress is the removal of molecules in the vapor phase. The response is the continued evaporation of the liquid to replace molecules in the vapor.

13-7 Vapor Pressure

Vapor molecules cannot escape when vaporization of a liquid occurs in a closed container. As more molecules leave the liquid, more gaseous molecules collide with the walls of the container, with one another, and with the liquid surface, so more condensation occurs. This condensation is responsible for the formation of liquid droplets that adhere to the sides of the vessel above a liquid surface and for the eventual establishment of equilibrium between liquid and vapor (see Figure 13-10b and c).

► Note the terminology: vapor pressure is measured as a *gas pressure* in equilibrium with a liquid, but we call it the *vapor pressure of the liquid*.

The partial pressure of vapor molecules above the surface of a liquid at equilibrium at a given temperature is the **vapor pressure (vp)** of the liquid at that temperature. Because the rate of evaporation increases with increasing temperature, vapor pressures of liquids *always* increase as temperature increases.

Vapor pressures can be measured with manometers (Figure 13-12). Easily vaporized liquids are called **volatile** liquids, and they have relatively high vapor pressures. The most volatile liquid in Table 13-4 is diethyl ether, whereas water is the least volatile.

Stronger cohesive forces tend to hold molecules in the liquid state. Methanol molecules are strongly linked by hydrogen bonding, whereas diethyl ether molecules are not, so methanol has a lower vapor pressure than diethyl ether. The very strong hydrogen bonding in water accounts for its unusually low vapor pressure (see Table 13-4) and high boiling point. Dispersion forces generally increase with increasing molecular size, so substances composed of larger molecules have lower vapor pressures.

We can understand the order of vapor pressures of some of the liquids cited in Table 13-4 and Figure 13-13 by considering the strengths of their intermolecular attractions. Water has the lowest vapor pressure (strongest cohesive forces) because each molecule has two hydrogen atoms to act as hydrogen-bond donors and each molecule can accept hydrogen bonds from two other molecules. Low-molecular-weight alcohols, such as methanol or ethanol, each have only one potential hydrogen-bond donor, so their average cohesive forces are weaker than those in water and their vapor pressures are higher. In benzene and diethyl

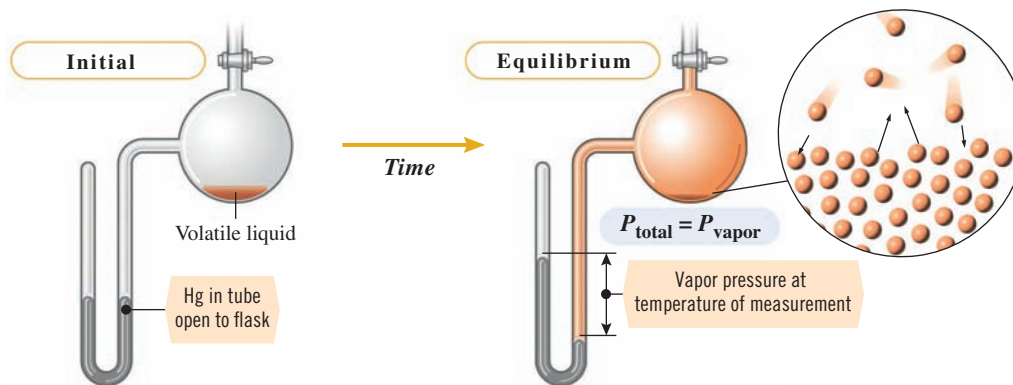
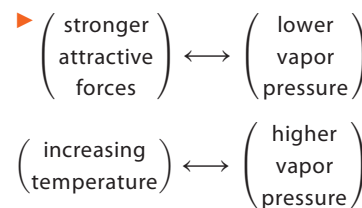


Figure 13-12 A representation of the measurement of vapor pressure of a liquid at a given temperature. The container is evacuated before the liquid is added. At the instant the liquid is added to the container, there are no molecules in the gas phase so the pressure is zero. Some of the liquid then vaporizes until equilibrium is established. The difference in heights of the mercury columns is a measure of the vapor pressure of the liquid at that temperature.

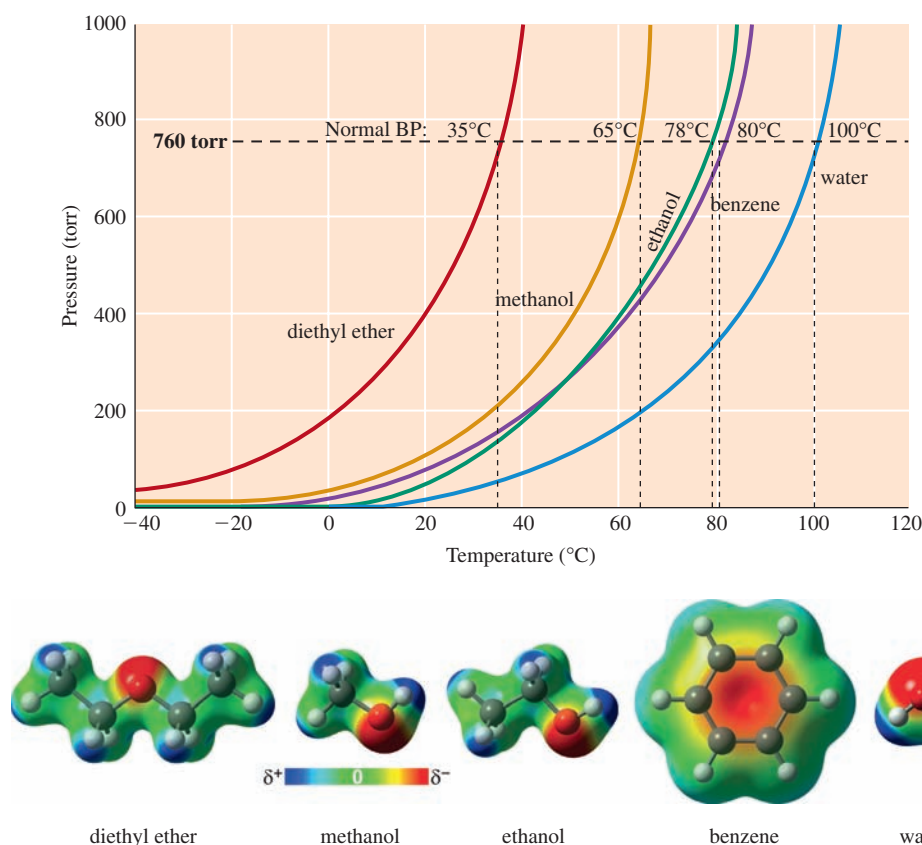


Figure 13-13 Plots of the vapor pressures of the liquids in Table 13-4. Notice that the increase in vapor pressure is *not* linear with temperature. Each substance exists as a liquid for temperatures and pressures to the left of its curve, and as a gas at conditions to the right of the curve. The *normal* boiling point of a liquid is the temperature at which its vapor pressure is equal to one atmosphere. The electrostatic charge potential surface for each molecule is also shown. These demonstrate the important role of polarity in reducing vapor pressure and increasing boiling points. Note the presence of partial positive charge on hydrogen atoms that are attached to the electronegative oxygen atoms. These can engage in hydrogen bonding to oxygen atoms in other molecules that have a build-up of partial negative charge.

Unless otherwise noted, all content on this page is © Cengage Learning.

► As long as some liquid remains in contact with the vapor, the pressure does not depend on the volume or surface area of the liquid.

Table 13-4 Vapor Pressure (in torr) of Some Liquids

	MW	0°C	25°C	50°C	75°C	100°C	125°C
diethyl ether	74 g/mol	185	470	1325	2680	4859	
methanol	32 g/mol	29.7	122	404	1126		
ethanol	46 g/mol	13	63	258	680		
benzene	78 g/mol	27.1	94.4	271	644	1360	
water	18 g/mol	4.6	23.8	92.5	300	760	1741

ether, the hydrogen atoms are all bonded to carbon, so strong hydrogen bonds are not possible. Electrons can move easily throughout the delocalized π -bonding orbitals of benzene, however, so benzene is quite polarizable and exhibits significant dispersion forces. In addition, the hydrogen atoms of benzene are more positively charged than most hydrogens that are bonded to carbon. The H atoms of benzene are attracted to the electron-rich π -bonding regions of nearby molecules. The accumulation of these forces gives benzene stronger cohesive forces, resulting in a lower vapor pressure than we might expect for a hydrocarbon. The diethyl ether molecule is only slightly polar, resulting in weak dipole–dipole forces and a high vapor pressure.

Generally speaking, the vapor pressure and boiling points of nonpolar molecules are related to their molecular weights and the size of the molecule. Heavier atoms have more electrons and are, therefore, more polarizable, giving rise to increased attractive dispersion forces between them. Bigger molecules with more surface area also have increased attractive dispersion forces and higher boiling points. Note that H_2O has the highest boiling point even though it is the smallest and lightest molecule in Table 13-4 and Figure 13-13. This is due to the stronger electrostatic attractions between polar molecules and the presence of hydrogen bonds.

► As water is being heated, but before it boils, small bubbles may appear in the container. This is not boiling, but rather the formation of bubbles of dissolved gases such as CO_2 and O_2 whose solubilities in water decrease with increasing temperature.

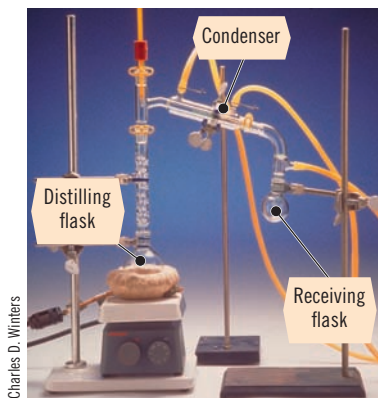


Figure 13-14 A laboratory setup for distillation. During distillation of an impure liquid, nonvolatile substances remain in the distilling flask. The liquid is vaporized and condensed before being collected in the receiving flask.

13-8 Boiling Points and Distillation

When heat energy is added to a liquid, it increases the kinetic energy of the molecules, and the temperature of the liquid increases. Heating a liquid always increases its vapor pressure. When a liquid is heated to a sufficiently high temperature under a given applied pressure (usually atmospheric), bubbles of vapor begin to form below the surface. If the vapor pressure inside the bubbles is less than the applied pressure on the surface of the liquid, the bubbles collapse as soon as they form. If the temperature is raised sufficiently, the vapor pressure is high enough that the bubbles can persist, rise to the surface, and burst, releasing the vapor into the air. This process is called *boiling* and is different from evaporation. The **boiling point** of a liquid is the temperature at which its vapor pressure equals the external pressure. The **normal boiling point** is the temperature at which the vapor pressure of a liquid is equal to exactly one atmosphere (760 torr). The vapor pressure of water is 760 torr at 100°C , its normal boiling point. As heat energy is added to a pure liquid *at its boiling point*, the temperature remains constant, because the energy is used to overcome the cohesive forces in the liquid to form vapor.

If the applied pressure is lower than 760 torr, say on a mountain, water boils below 100°C . The chemical reactions involved in cooking food occur more slowly at the lower temperature, so it takes longer to cook food in boiling water at high altitudes than at sea level. A pressure cooker cooks food rapidly because water boils at higher temperatures under increased pressures. The higher temperature of the boiling water increases the rate of cooking.

The vapor pressure of any given liquid depends *only* on the temperature of the liquid.

The boiling point of any given liquid depends *only* on the external pressure.

Different liquids have different cohesive forces, so they have different vapor pressures and boil at different temperatures. A mixture of liquids with sufficiently different boiling points can often be separated into its components by **distillation**. In this process the mixture is heated slowly until the temperature reaches the point at which the most volatile liquid boils off. If this component is a liquid under ordinary conditions, it is subsequently recondensed in a water-cooled condensing column (Figure 13-14) and collected as a distillate. After enough heat has been added to vaporize all of the most volatile liquid, the temperature again rises slowly until the boiling point of the next substance is reached, and the process continues. Any nonvolatile substances dissolved in the liquid do not boil, but remain in the distilling flask. Impure water can be purified and separated from its dissolved salts by distillation. Compounds with similar boiling points, especially those that interact very strongly with one another, are not effectively separated by simple distillation, but require a modification called fractional distillation (see Section 14-10).

13-9 Heat Transfer Involving Liquids

Heat must be added to a liquid to raise its temperature (see Section 1-14). The **specific heat** ($\text{J/g} \cdot ^\circ\text{C}$) or **molar heat capacity** ($\text{J/mol} \cdot ^\circ\text{C}$) of a liquid is the amount of heat that must be added to the stated mass of liquid to raise its temperature by one degree Celsius. If heat is added to a pure liquid under constant pressure, the temperature rises until its boiling point is reached. Then the temperature remains constant until enough heat has been added to boil away all the liquid. The **molar heat** (or **enthalpy**) of **vaporization** (ΔH_{vap}) of a liquid is the amount of heat that must be added to one mole of the liquid at its boiling point to convert it to vapor with no change in temperature. Heats of vaporization can also be expressed as energy per gram. For example, the heat of vaporization for water at its boiling point is 40.7 kJ/mol , or $2.26 \times 10^3 \text{ J/g}$:

$$\frac{? \text{ J}}{\text{g}} = \frac{40.7 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1 \text{ mol}}{18.0 \text{ g}} = 2.26 \times 10^3 \text{ J/g}$$

Like many other properties of liquids, heats of vaporization reflect the strengths of intermolecular forces. Heats of vaporization generally increase as boiling points and intermolecular forces increase and as vapor pressures decrease. Table 13-5 illustrates this. The high heats of vaporization of water, ethylene glycol, and ethyl alcohol are due mainly to the strong hydrogen-bonding interactions in these liquids (see Section 13-2). The very high value for water makes it quite effective as a coolant and, in the form of steam, as a source of heat.

Liquids can evaporate even below their boiling points. The water in perspiration is an effective coolant for our bodies. Each gram of water that evaporates absorbs 2.41 kJ of heat from the body. We feel even cooler in a breeze because perspiration evaporates faster, so heat is removed more rapidly.

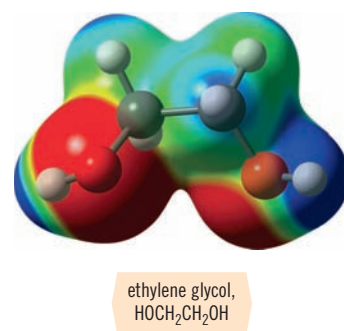
► The specific heat and heat capacity of a substance change somewhat with its temperature. For most substances, this variation is small enough to ignore.

► Molar heats of vaporization (also called molar *enthalpies* of vaporization) are often expressed in kilojoules rather than joules. The units of heat of vaporization do *not* include temperature. This is because boiling occurs with *no change in temperature*.

► The heat of vaporization of water is higher at 37°C (normal body temperature) than at 100°C (2.41 kJ/g compared to 2.26 kJ/g).

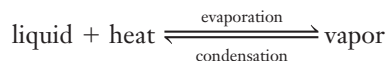
Table 13-5 Heats of Vaporization, Boiling Points, and Vapor Pressures of Some Common Liquids

Liquid	Molecular Weight (g/mol)	Vapor Pressure (torr at 20°C)	Boiling Point at 1 atm ($^\circ\text{C}$)	Heat of Vaporization at Boiling Point	
				J/g	kJ/mol
diethyl ether, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	74	442.	34.6	351	26.0
carbon tetrachloride, CCl_4	153	85.6	76.8	213	32.8
ethanol, $\text{CH}_3\text{CH}_2\text{OH}$	46	43.9	78.3	855	39.3
benzene, C_6H_6	78	74.6	80.1	395	30.8
water, H_2O	18	17.5	100.	2260	40.7
ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$	62	0.1	197.3	984	58.9



Unless otherwise noted, all content on this page is © Cengage Learning.

Condensation is the reverse of evaporation. The amount of heat that must be removed from a vapor to condense it (without change in temperature) is called the **heat of condensation**.



The heat of condensation of a liquid is equal in magnitude to the heat of vaporization. It is released by the vapor during condensation.

Because 2.26 kJ must be absorbed to vaporize one gram of water at 100°C, that same amount of heat must be released to the environment when one gram of steam at 100°C condenses to form liquid water at 100°C. In steam-heated radiators, steam condenses and releases 2.26 kJ of heat per gram as its molecules collide with the cooler radiator walls and condense there. The metallic walls conduct heat well. They transfer the heat to the air in contact with the outside walls of the radiator. The heats of condensation and vaporization of non-hydrogen-bonded liquids, such as benzene, have smaller magnitudes than those of hydrogen-bonded liquids (see Table 13-5). They are, therefore, much less effective as heating and cooling agents.

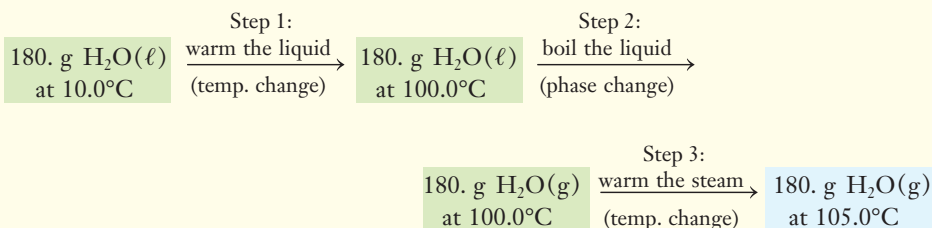
► Because of the large amount of heat released by steam as it condenses, burns caused by steam at 100°C are much more severe than burns caused by liquid water at 100°C.

EXAMPLE 13-2 Heat of Vaporization

Calculate the amount of heat, in joules, required to convert 180. grams of water at 10.0°C to steam at 105.0°C.

Plan

The total amount of heat absorbed is the sum of the amounts required to (1) warm the liquid water from 10.0°C to 100.0°C, (2) convert the liquid water to steam at 100.0°C, and (3) warm the steam from 100.0°C to 105.0°C.



Steps 1 and 3 involve the specific heats of water and steam, 4.18 J/g · °C and 2.03 J/g · °C, respectively (see Appendix E), whereas step 2 involves the heat of vaporization of water (2.26 × 10³ J/g).

Solution

$$\begin{array}{l} 1. \quad \underline{} \text{ J} = 180. \text{ g} \times \frac{4.18 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times (100.0^\circ\text{C} - 10.0^\circ\text{C}) = 6.77 \times 10^4 \text{ J} = 0.677 \times 10^5 \text{ J} \\ 2. \quad \underline{} \text{ J} = 180. \text{ g} \times \frac{2.26 \times 10^3 \text{ J}}{\text{g}} = 4.07 \times 10^5 \text{ J} \\ 3. \quad \underline{} \text{ J} = 180. \text{ g} \times \frac{2.03 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times (105.0^\circ\text{C} - 100.0^\circ\text{C}) = 1.8 \times 10^3 \text{ J} = 0.018 \times 10^5 \text{ J} \end{array}$$

$$\text{Total amount of heat absorbed} = 4.76 \times 10^5 \text{ J}$$

You should now work Exercises 50 and 51.

STOP & THINK

Far more heat is associated with the phase change than with the warming of liquid or steam.

Distillation is not an economical way to purify large quantities of water for public water supplies. The high heat of vaporization of water requires a large amount of energy, making it too expensive to vaporize large volumes of water.

Problem-Solving Tip Temperature Change or Phase Change?

A problem such as Example 13-2 can be broken down into steps so that each involves *either* a temperature change *or* a phase change, but not both. A temperature change calculation uses the specific heat of the substance (steps 1 and 3 of Example 13-2); remember that each different phase has its own specific heat. Note also that because we are using ΔT (change in temperature) we do not need to convert $^{\circ}\text{C}$ to kelvin. A phase change always takes place with *no change* in temperature, so that calculation does not involve temperature (step 2 of Example 13-2).

EXAMPLE 13-3 Heat of Vaporization

Compare the amount of “cooling” experienced by an individual who drinks 400. mL of ice water (0.0°C) with the amount of “cooling” experienced by an individual who “sweats out” 400. mL of water. Assume that the sweat is essentially pure water and that all of it evaporates. The density of water is very nearly 1.00 g/mL at both 0.0°C and 37.0°C , average body temperature. The heat of vaporization of water is 2.41 kJ/g at 37.0°C .

Plan

In the case of drinking ice water, the body is cooled by the amount of heat required to raise the temperature of 400. mL (400. g) of water from 0.0°C to 37.0°C . The amount of heat lost by perspiration is equal to the amount of heat required to vaporize 400. g of water at 37.0°C .

Solution

Raising the temperature of 400. g of water from 0.0°C to 37.0°C requires

$$Q = (400.\text{ g})(4.18\text{ J/g}\cdot^{\circ}\text{C})(37.0^{\circ}\text{C}) = 6.19 \times 10^4\text{ J, or } 61.9\text{ kJ}$$

Evaporating (i.e., “sweating out”) 400. mL of water at 37°C requires

$$Q = (400.\text{ g})(2.41 \times 10^3\text{ J/g}) = 9.64 \times 10^5\text{ J, or } 964\text{ kJ}$$

Thus, we see that “sweating out” 400. mL of water removes 964 kJ of heat from one’s body, whereas drinking 400. mL of ice water removes only 61.9 kJ. Stated differently, sweating removes $(964/61.9)$ or 15.6 times more heat than drinking ice water!

You should now work Exercise 55.



As Example 13-3 illustrates, perspiration is more effective at cooling the body than drinking cold fluids. For health reasons, however, it is important to replace the water lost by perspiration.

ENRICHMENT

The Clausius–Clapeyron Equation

We have seen (see Figure 13-13) that vapor pressure increases with increasing temperature. Let us now discuss the quantitative expression of this relationship.

When the temperature of a liquid is changed from T_1 to T_2 , the vapor pressure of the liquid changes from P_1 to P_2 . These changes are related to the molar heat of vaporization, ΔH_{vap} , for the liquid by the **Clausius–Clapeyron equation**.

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Although ΔH_{vap} changes somewhat with temperature, it is usually adequate to use the value tabulated at the normal boiling point of the liquid (see Appendix E) unless more precise values are available. The units of R must be consistent with those of ΔH_{vap} .

► The Clausius–Clapeyron equation is used for three types of calculations: (1) to predict the vapor pressure of a liquid at a specified temperature, as in Example 13-4; (2) to determine the temperature at which a liquid has a specified vapor pressure; and (3) to calculate ΔH_{vap} from measurement of vapor pressures at different temperatures.

EXAMPLE 13-4 Vapor Pressure Versus Temperature

The normal boiling point of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is 78.3°C , and its molar heat of vaporization is 39.3 kJ/mol (see Appendix E). What would be the vapor pressure, in torr, of ethanol at 50.0°C ?

Plan

The normal boiling point of a liquid is the temperature at which its vapor pressure is 760 torr, so we designate this as one of the conditions (subscript 1). We wish to find the vapor pressure at another temperature (subscript 2), and we know the molar heat of vaporization. We use the Clausius–Clapeyron equation to solve for P_2 .

Solution

$$P_1 = 760 \text{ torr} \quad \text{at} \quad T_1 = 78.3^\circ\text{C} + 273.2 = 351.5 \text{ K}$$

$$P_2 = ? \quad \text{at} \quad T_2 = 50.0^\circ\text{C} + 273.2 = 323.2 \text{ K}$$

$$\Delta H_{\text{vap}} = 39.3 \text{ kJ/mol} \quad \text{or} \quad 3.93 \times 10^4 \text{ J/mol}$$

We solve for P_2 .

$$\ln\left(\frac{P_2}{760 \text{ torr}}\right) = \frac{3.93 \times 10^4 \text{ J/mol}}{\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)} \left(\frac{1}{351.5 \text{ K}} - \frac{1}{323.2 \text{ K}}\right)$$

$$\ln\left(\frac{P_2}{760 \text{ torr}}\right) = -1.18 \quad \text{so} \quad \left(\frac{P_2}{760 \text{ torr}}\right) = e^{-1.18} = 0.307$$

$$P_2 = 0.307(760 \text{ torr}) = 233 \text{ torr} \quad (\text{Note: lower vapor pressure at lower temperature})$$

You should now work Exercise 58.

Table 13-6 General Effects of Intermolecular Attractions on Physical Properties of Liquids

Property	Volatile Liquids (weak intermolecular attractions)	Nonvolatile Liquids (strong intermolecular attractions)
cohesive forces	low	high
viscosity	low	high
surface tension	low	high
specific heat	low	high
vapor pressure	high	low
rate of evaporation	high	low
boiling point	low	high
heat of vaporization	low	high

We have described many properties of liquids and discussed how they depend on intermolecular forces of attraction. The general effects of these attractions on the physical properties of liquids are summarized in Table 13-6. “High” and “low” are relative terms. Table 13-6 is intended to show only very general trends. Example 13-5 illustrates the use of intermolecular attractions to predict boiling points.

EXAMPLE 13-5 Boiling Points Versus Intermolecular Forces

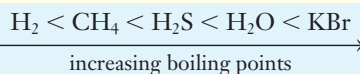
Predict the order of increasing boiling points for the following: H_2S ; H_2O ; CH_4 ; H_2 ; KBr .

Plan

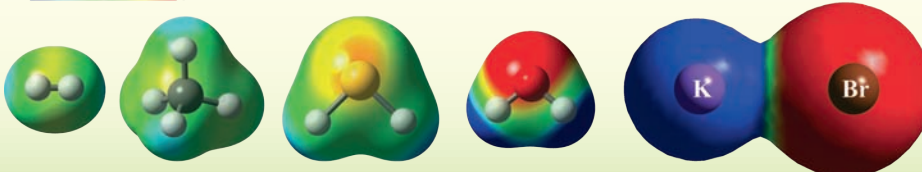
We analyze the polarity and size of each substance to determine the kinds of intermolecular forces that are present. In general, the stronger the intermolecular forces, the higher is the boiling point of the substance.

Solution

KBr is ionic, so it boils at the highest temperature. Water exhibits strong hydrogen bonding and boils at the next highest temperature. Hydrogen sulfide is the only other polar covalent substance in the list, so it boils below H_2O but above the other two substances. Both CH_4 and H_2 are nonpolar. The larger CH_4 molecule is more easily polarized than the very small H_2 molecule, so dispersion forces are stronger in CH_4 . Thus, CH_4 boils at a higher temperature than H_2 .



δ^+  δ^-

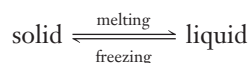


You should now work Exercise 22.

The Solid State

13-10 Melting Point

The **melting point (freezing point)** of a substance is the temperature at which its solid and liquid phases coexist in equilibrium.



The *melting point* of a solid is the same as the *freezing point* of its liquid. It is the temperature at which the rate of melting of a solid is the same as the rate of freezing of its liquid under a given applied pressure.

The **normal melting point** of a substance is its melting point at one atmosphere pressure. Changes in pressure have very small effects on melting points, but they have large effects on boiling points.

13-11 Heat Transfer Involving Solids

When heat is added to a solid below its melting point, its temperature rises. After enough heat has been added to bring the solid to its melting point, additional heat is required to convert the solid to liquid. During this melting process, the temperature remains constant at the melting point until all of the substance has melted. After melting is complete, the continued addition of heat results in an increase in the temperature of the liquid, until the boiling point is reached. This is illustrated graphically in the first three segments of the heating curve in Figure 13-15.

► Melting is always endothermic. The term “fusion” means “melting.”

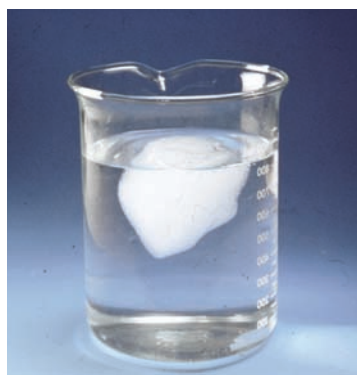
The **molar heat (or enthalpy) of fusion** (ΔH_{fus} ; kJ/mol) is the amount of heat required to melt one mole of a solid at its melting point. Heats of fusion can also be expressed on a per gram basis. The heat of fusion depends on the *intermolecular* forces of attraction in the solid state. These forces “hold the molecules together” as a solid. Heats of fusion are *usually* higher for substances with higher melting points. Values for some common compounds are shown in Table 13-7. Appendix E has more values.

Table 13-7 Some Melting Points and Heats of Fusion

Substance	Melting Point (°C)	Heat of Fusion	
		J/g	kJ/mol
methane, CH ₄	−182	58.6	0.92
ethanol, CH ₃ CH ₂ OH	−117	109	5.02
water, H ₂ O	0	334	6.02
naphthalene, C ₁₀ H ₈	80.2	147	18.8
silver nitrate, AgNO ₃	209	67.8	11.5
aluminum, Al	658	395	10.6
sodium chloride, NaCl	801	519	30.3



Charles D. Winters



Charles D. Winters

During any phase change,
 $\text{liquid} \rightleftharpoons \text{gas}$
 and
 $\text{solid} \rightleftharpoons \text{liquid}$
 the temperature remains constant.

Unless otherwise noted, all content on this page is © Cengage Learning.

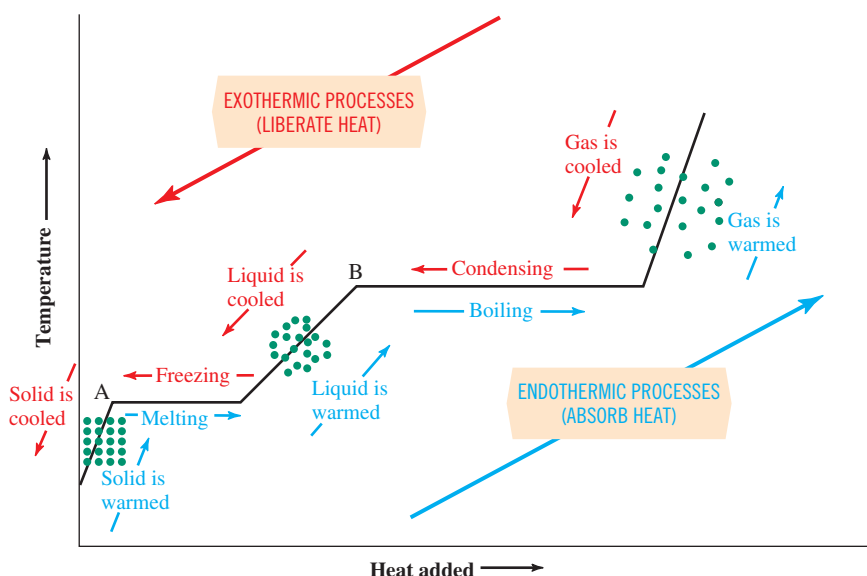
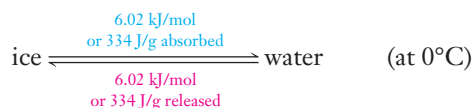


Figure 13-15 A typical heating curve at constant pressure. When heat energy is added to a solid below its melting point, the temperature of the solid rises until its melting point is reached (point A). In this region of the plot, the slope is rather steep because of the low specific heats of solids [e.g., $2.09 \text{ J/g} \cdot ^\circ\text{C}$ for $\text{H}_2\text{O}(\text{s})$]. If additional heat energy is added to the solid at its melting point (A), its temperature remains constant until all of the solid has melted, because the melting process requires energy. The length of this horizontal line is proportional to the heat of fusion of the substance—the higher the heat of fusion, the longer the line. When all of the solid has melted, further heating of the liquid raises its temperature until its boiling point is reached (point B). The slope of this line is less steep than that for warming the solid, because the specific heat of the liquid phase [e.g., $4.18 \text{ J/g} \cdot ^\circ\text{C}$ for $\text{H}_2\text{O}(\ell)$] is usually greater than that of the corresponding solid. If heat is added to the liquid at its boiling point (B), the added heat energy is absorbed as the liquid boils and the temperature remains constant until all of the liquid has boiled. This horizontal line is longer than the previous one, because the heat of vaporization of a substance is always higher than its heat of fusion. When all of the liquid has been converted to a gas (vapor), the addition of more heat raises the temperature of the gas. This segment of the plot has a steep slope because of the relatively low specific heat of the gas phase [e.g., $2.03 \text{ J/g} \cdot ^\circ\text{C}$ for $\text{H}_2\text{O}(\text{g})$]. Each step in the process can be reversed by removing the same amount of heat.

The **heat (or enthalpy) of solidification** of a liquid is equal in magnitude to the heat of fusion. It represents removal of a sufficient amount of heat from a given amount (1 mol or 1 g) of liquid to solidify the liquid at its freezing point. For water,



EXAMPLE 13-6 Heat of Fusion

The molar heat of fusion, ΔH_{fus} , of Na is 2.6 kJ/mol at its melting point, 97.5°C. How much heat must be absorbed by 5.0 g of solid Na at 97.5°C to melt it?

Plan

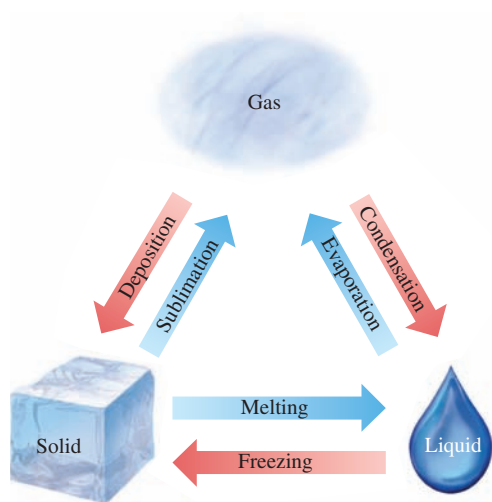
Melting takes place at a constant temperature. The molar heat of fusion tells us that every mole of Na, 23 grams, absorbs 2.6 kJ of heat at 97.5°C during the melting process. We want to know the amount of heat that 5.0 grams would absorb. We use the appropriate unit factors, constructed from the atomic weight and ΔH_{fus} , to find the amount of heat absorbed.

Solution

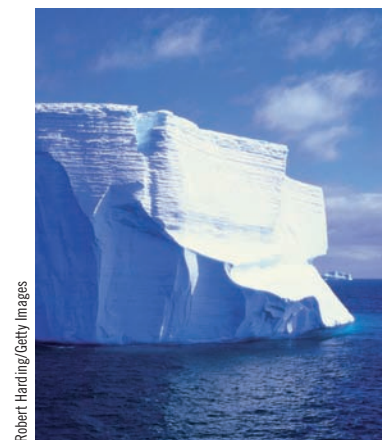
$$\underline{?} \text{ kJ} = 5.0 \text{ g Na} \times \frac{1 \text{ mol Na}}{23 \text{ g Na}} \times \frac{2.6 \text{ kJ}}{1 \text{ mol Na}} = \underline{0.57 \text{ kJ}}$$

STOP & THINK

Melting takes place at constant temperature, so temperature does not appear in this calculation, as the units of ΔH_{fus} show. The mass of Na given (5.0 g) is smaller than the atomic weight of Na (23 g/mol), so the answer (0.57 kJ) is smaller than the molar heat of fusion.



Transitions among the three states of matter. The transitions shown in blue are endothermic (absorb heat); those shown in red are exothermic (release heat). Water vapor is invisible; we can see clouds because they contain tiny droplets of liquid water in equilibrium with water vapor.



Robert Harding/Getty Images

EXAMPLE 13-7 Heat of Fusion

Calculate the amount of heat that must be absorbed by 50.0 grams of ice at -12.0°C to convert it to water at 20.0°C . Refer to Appendix E.

Plan

We must determine the amount of heat absorbed during three steps: (1) warming 50.0 g of ice from -12.0°C to its melting point, 0.0°C (we use the specific heat of ice, $2.09 \text{ J/g} \cdot ^\circ\text{C}$); (2) melting the ice with no change in temperature (we use the heat of fusion of ice at 0.0°C , 334 J/g ; and (3) warming the resulting liquid from 0.0°C to 20.0°C (we use the specific heat of water, $4.18 \text{ J/g} \cdot ^\circ\text{C}$).

► Ice is very efficient for cooling because considerable heat is required to melt a given mass of it. However, ΔH_{vap} is generally much greater than ΔH_{fusion} , so evaporative cooling is preferable when possible.

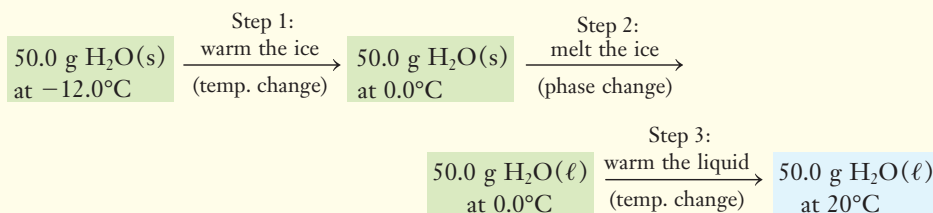
STOP & THINK

It is important to know the melting and boiling point temperatures for the material in question. We must always treat a phase change as a separate part of the heat calculation.

► Step 1: Temperature change only

► Step 2: Phase change only

► Step 3: Temperature change only

**Solution**

$$1. 50.0 \text{ g} \times \frac{2.09 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times [0.0 - (-12.0)]^\circ\text{C} = 1.25 \times 10^3 \text{ J} = 0.125 \times 10^4 \text{ J}$$

$$2. 50.0 \text{ g} \times \frac{334 \text{ J}}{\text{g}} = 1.67 \times 10^4 \text{ J}$$

$$3. 50.0 \text{ g} \times \frac{4.18 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times (20.0 - 0.0)^\circ\text{C} = 4.18 \times 10^3 \text{ J} = 0.418 \times 10^4 \text{ J}$$

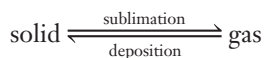
$$\text{Total amount of heat absorbed} = 2.21 \times 10^4 \text{ J} = 22.1 \text{ kJ}$$

Note that most of the heat was absorbed in step 2, melting the ice.

You should now work Exercise 56.

13-12 Sublimation and the Vapor Pressure of Solids

Some solids, such as iodine and carbon dioxide, vaporize at atmospheric pressure without passing through the liquid state. This process is known as **sublimation**. Solids exhibit vapor pressures just as liquids do, but they generally have much lower vapor pressures. Solids with high vapor pressures sublime easily. The characteristic odor of a common household solid, *para*-dichlorobenzene (moth repellent), is due to sublimation. The reverse process, by which a vapor solidifies without passing through the liquid phase, is called **deposition**.



Some impure solids can be purified by sublimation and subsequent deposition of the vapor (as a solid) onto a cooler surface. Purification of iodine by sublimation is illustrated in Figure 13-16.

13-13 Phase Diagrams (*P* versus *T*)

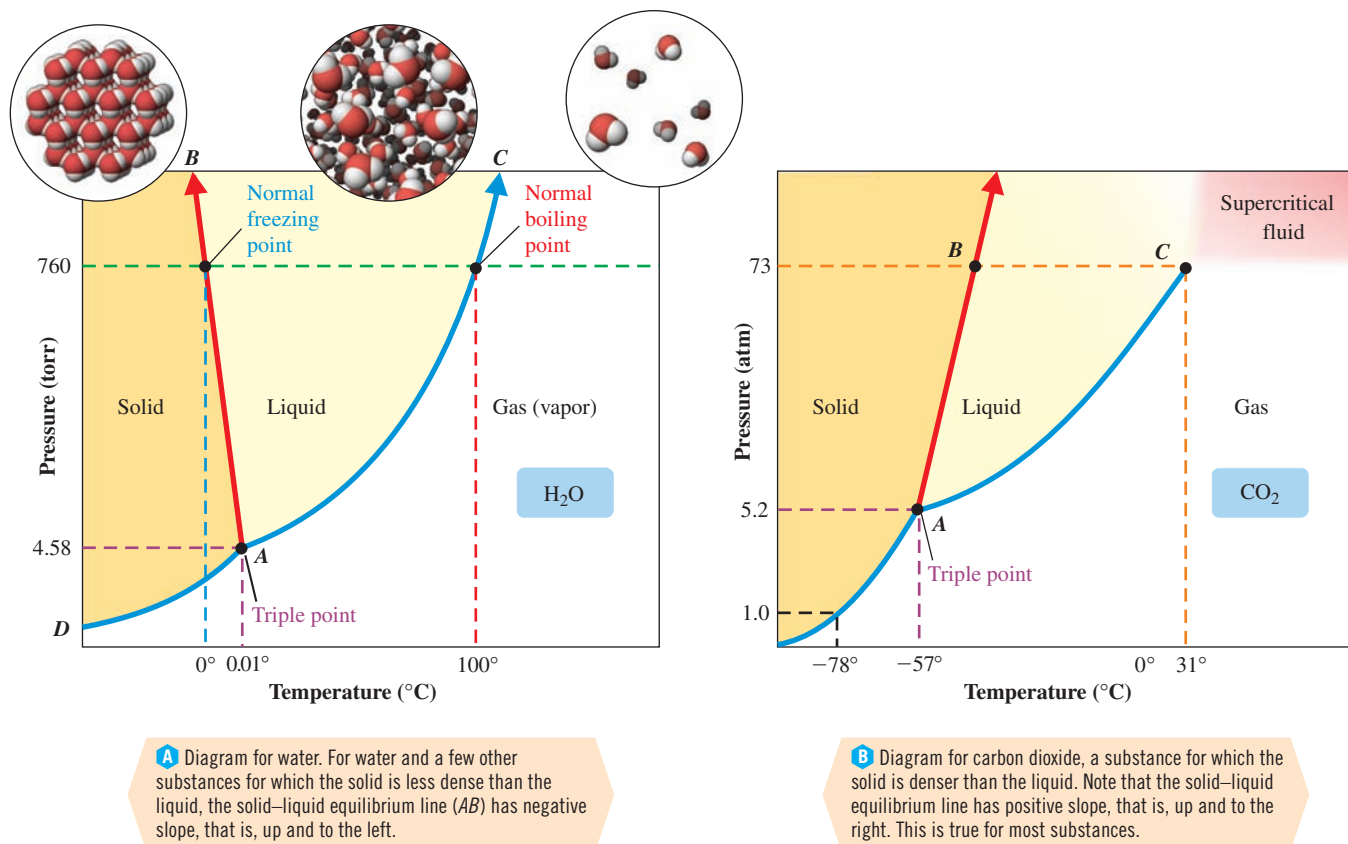
We have discussed the general properties of the three phases of matter. Now we can describe **phase diagrams** that show the equilibrium pressure–temperature relationships among the different phases of a given pure substance in a closed system. Our discussion of phase diagrams applies only to *closed systems* (e.g., a sample in a sealed container), in which matter does not escape into the surroundings. This limitation is especially important when the vapor phase is involved. Figure 13-17 shows a portion of the phase diagrams for water and carbon dioxide. The curves are not drawn to scale. The distortion allows us to describe the changes of state over wide ranges of pressure or temperature using one diagram.

The curved line from *A* to *C* in Figure 13-17a is a vapor pressure curve obtained experimentally by measuring the vapor pressures of water at various temperatures (Table 13-8). Points along this curve represent the temperature–pressure combinations for which liquid and gas (vapor) coexist in equilibrium. At points above *AC*, the stable form of water is liquid; below the curve, it is vapor.



Figure 13-16 Sublimation can be used to purify volatile solids. Iodine, I₂, sublimates readily to form purple I₂ vapor. The high vapor pressure of the solid I₂ in the lower mixture causes it to sublime when heated. Crystals of purified iodine are formed when the vapor is deposited to form solid on the cooler (upper) portion of the apparatus.

Unless otherwise noted, all content on this page is © Cengage Learning.



A.A. Clifford, K.D. Bartle, and C.M. Rayner, Department of Chemistry, University of Leeds, Leeds, LS29JT

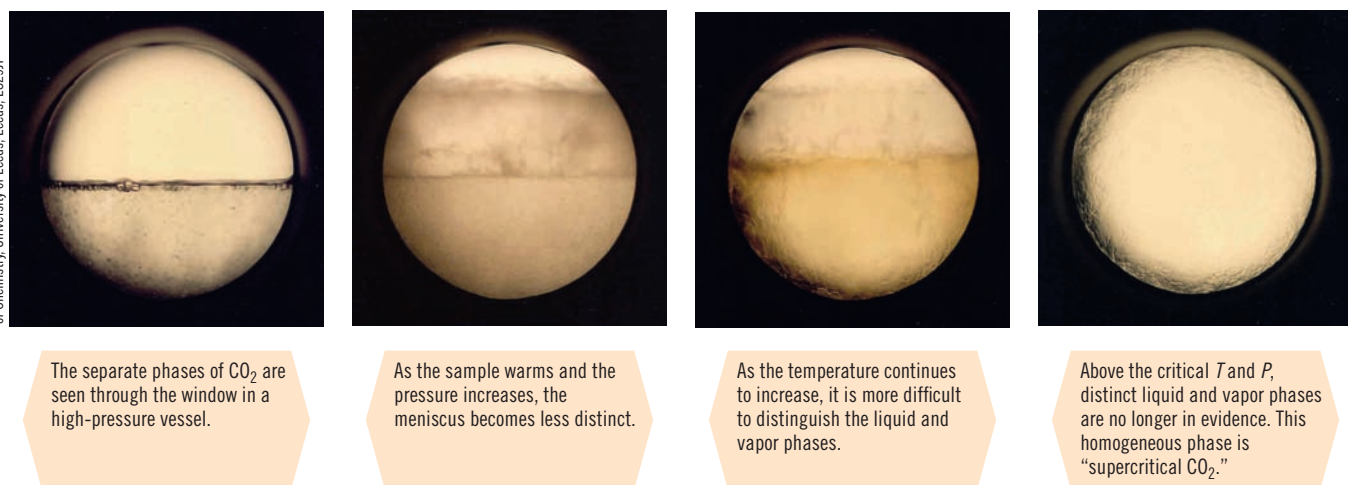


Figure 13-17 Phase diagrams (not to scale).

Line AB represents the liquid–solid equilibrium conditions. We see that this line has a negative slope (up and to the left). Water is one of the very few substances for which this is the case. The negative slope indicates that increasing the pressure sufficiently on the surface of ice causes it to melt. This is because ice is *less dense* than liquid water in the vicinity of the liquid–solid equilibrium. The network of hydrogen bonding in ice is more extensive than that in liquid water and requires a greater separation of H_2O molecules. This causes ice to float in liquid water. Almost all other solids are denser than their corresponding liquids; they would have positive slopes associated with line AB . The stable form of water at points to the left of AB is solid (ice). Thus AB is called a *melting curve*.

▶ The CO_2 in common fire extinguishers is liquid. As you can see from Figure 13-17b, the liquid must be at some pressure greater than 10 atm for temperatures above 0°C . It is ordinarily at about 65 atm (more than 900 lb/in.²), so these cylinders must be *handled with care*.

Unless otherwise noted, all content on this page is © Cengage Learning.

Charles D. Winters



Benzene is *denser* as a solid than as a liquid, so the solid sinks in the liquid (*left*). This is the behavior shown by nearly all known substances except water (*right*).

Charles D. Winters



Water is one of the few compounds that expands when it freezes. This expansion on freezing can lead to the breaking of sealed containers that are too full of water.

► Phase diagrams are obtained by combining the results of heating curves measured experimentally at different pressures.

► A fluid *below* its critical temperature may properly be identified as a liquid or as a gas. *Above* the critical temperature, we should use the term “fluid.”

Table 13-8 Points on the Vapor Pressure Curve for Water

temperature (°C)	−10.	0	20	30	50	70	90	95	100	101
vapor pressure (torr)	2.1	4.6	17.5	31.8	92.5	234	526	634	760	788

There is only one point, *A*, at which all three phases of a substance—solid, liquid, and gas—can coexist at equilibrium. This is called the **triple point**. For water it occurs at 4.6 torr and 0.01°C.

At pressures below the triple-point pressure, the liquid phase does not exist; rather, the substance goes directly from solid to gas (sublimes) or the reverse happens (crystals deposit from the gas). At pressures and temperatures along *AD*, the *sublimation curve*, solid and vapor are in equilibrium.

Consider CO₂ (see Figure 13-17b). The triple point is at 5.2 atmospheres and −57°C. This pressure is *above* normal atmospheric pressure, so liquid CO₂ cannot exist at atmospheric pressure. Dry ice (solid CO₂) sublimates and does not melt at atmospheric pressure.

The **critical temperature** is the temperature above which a gas cannot be liquefied, that is, the temperature above which the liquid and gas do not exist as distinct phases. A substance at a temperature above its critical temperature is called a **supercritical fluid**. The **critical pressure** is the pressure required to liquefy a gas (vapor) *at* its critical temperature. The combination of critical temperature and critical pressure is called the **critical point** (*C* in Figure 13-17). For H₂O, the critical point is at 374°C and 218 atmospheres; for CO₂, it is at 31°C and 73 atmospheres. There is no such upper limit to the solid–liquid line, however, as emphasized by the arrowhead at the top of that line.

To illustrate the use of a phase diagram in determining the physical state or states of a system under different sets of pressures and temperatures, let's consider a sample of water at point *E* in Figure 13-18a (355 torr and −10°C). At this point all the water is in the form of ice, H₂O(s). Suppose that we hold the pressure constant and gradually increase the temperature—in other words, trace a path from left to right along *EH*. At the temperature *F* at which *EH* intersects *AB* (the melting curve) some of the ice melts. If we stopped here, equilibrium between solid and liquid water would eventually be established, and both phases would be present. If we added more heat, all the solid would melt with no temperature change. Remember that all phase changes of pure substances occur at constant temperature.

Once the solid is completely melted, additional heat causes the temperature to rise. Eventually, at point *G* (355 torr and 80°C), some of the liquid begins to boil; liquid, H₂O(l), and vapor, H₂O(g), are in equilibrium. Adding more heat at constant pressure vaporizes the rest of the water with no temperature change. Adding still more heat warms the vapor (gas) from *G* to *H*. Complete vaporization would also occur if, at point *G* and before all the liquid had vaporized, the temperature were held constant and the pressure were decreased to, say, 234 torr at point *I*. If we wished to hold the pressure at 234 torr and condense some of the vapor, it would be necessary to cool the vapor to 70°C, point *J*, which lies on the vapor pressure curve, *AC*. To state this in another way, the vapor pressure of water at 70°C is 234 torr.

Suppose we move back to solid at point *E* (355 torr and −10°C). If we now hold the temperature at −10°C and reduce the pressure, we move vertically down along *EK*. At a pressure of 2.1 torr we reach the sublimation curve, at which point the solid passes directly into the gas phase (sublimes) until all the ice has sublimed. An important application of this phenomenon is in the freeze-drying of foods. In this process a water-containing food is cooled below the freezing point of water to form ice, which is then removed as a vapor by decreasing the pressure.

Let's clarify the nature of the fluid phases (liquid and gas) and of the critical point by describing two different ways that a gas can be liquefied. A sample at point *W* in the phase diagram of Figure 13-18b is in the vapor (gas) phase, below its critical temperature. Suppose we compress the sample at constant *T* from point *W* to point *Z*. We can identify a definite pressure (the intersection of line *WZ* with the vapor pressure curve *AC*) where the transition from gas to liquid takes place. If we go *around* the critical point by the path *WXYZ*, however, no such clear-cut transition takes place. By this second path, the density

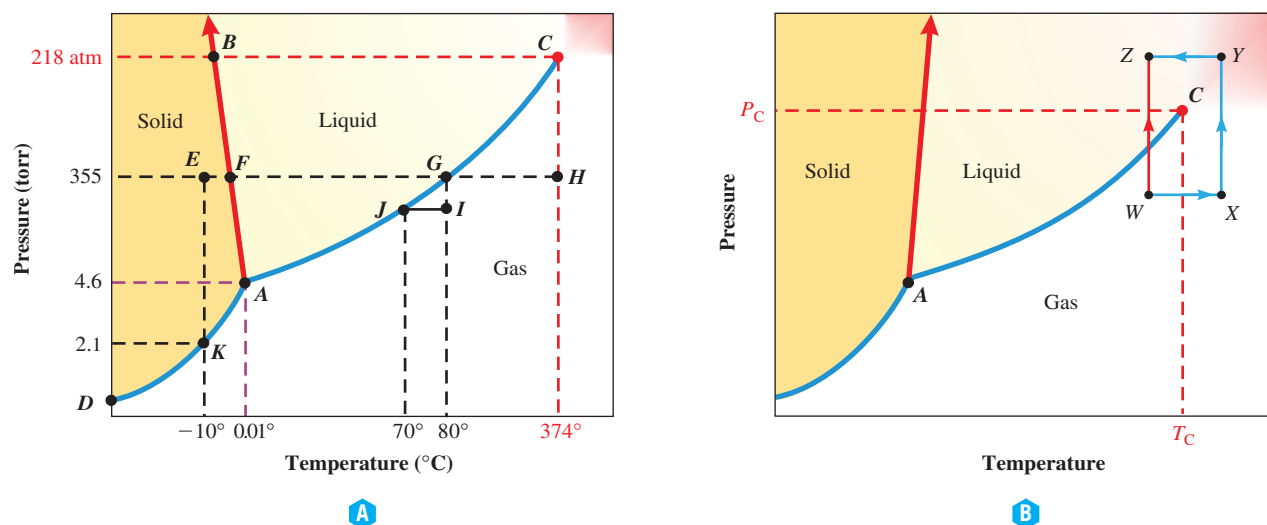


Figure 13-18 Some interpretations of phase diagrams. (a) The phase diagram of water. Phase relationships at various points in this diagram are described in the text. (b) Two paths by which a gas can be liquefied. (1) Below the critical temperature. Compressing the sample at *constant* temperature is represented by the vertical line WZ. Where this line crosses the vapor pressure curve AC, the gas liquefies; at that set of conditions, *two distinct phases*, gas and liquid, are present in equilibrium with each other. These two phases have different properties, for example, different densities. Raising the pressure further results in a completely liquid sample at point Z. (2) Above the critical temperature. Suppose that we instead first warm the gas at constant pressure from W to X, a temperature above its critical temperature. Then, holding the temperature constant, we increase the pressure to point Y. Along this path, the sample increases *smoothly* in density, with no sharp transition between phases. From Y, we then decrease the temperature to reach final point Z, where the sample is clearly a liquid.

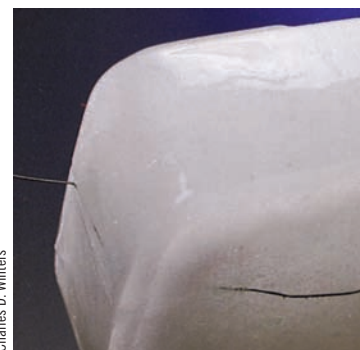
and other properties of the sample vary in a continuous manner; there is no definite point at which we can say that the sample changes from gas to liquid (see Figure 13-17c).

13-14 Amorphous Solids and Crystalline Solids

We have already seen that solids have definite shapes and volumes, are not very compressible, are dense, and diffuse only very slowly into other solids. They are generally characterized by compact, ordered arrangements of particles that vibrate about fixed positions in their structures.

Some noncrystalline solids, called **amorphous solids**, have no well-defined, ordered structure. Examples include rubber, some kinds of plastics, glass, and amorphous sulfur. Some amorphous solids are called “glasses” because, like liquids, they flow, although *very* slowly. The irregular structures of glasses are intermediate between those of freely flowing liquids and those of crystalline solids; there is only short-range order. Crystalline solids such as ice and sodium chloride have well-defined, sharp melting temperatures. Particles in amorphous solids are irregularly arranged, so intermolecular forces among their particles vary in strength within a sample. Melting occurs at different temperatures for various portions of the same sample as the intermolecular forces are overcome. Unlike crystalline solids, glasses and other amorphous solids do not exhibit sharp melting points, but soften over a temperature range.

The shattering of a crystalline solid can produce fragments having the same (or related) interfacial angles and structural characteristics as the original sample. The shattering of a cube of rock salt often produces several smaller cubes of rock salt. Such cleaving occurs preferentially along the crystal lattice planes between which the interionic or intermolecular forces of attraction are weakest. Amorphous solids with irregular structures, such as glasses, shatter irregularly to yield pieces with curved edges and irregular angles.



A weighted wire cuts through a block of ice. The ice melts under the high pressure of the wire, and then refreezes behind the wire.

► One test for the purity of a crystalline solid is the sharpness of its melting point. Impurities alter the intermolecular forces and cause melting to occur over a considerable temperature range.

Unless otherwise noted, all content on this page is © Cengage Learning.



Charles D. Winters

The regular external shape of a crystal is the result of the regular internal arrangements of its atoms, molecules, or ions. The crystal shown is quartz.

► William and Lawrence Bragg are the only father and son to receive the Nobel Prize, which they shared in physics in 1915.

► The lattice planes are planes within the crystal containing regularly ordered arrangements of particles.

ENRICHMENT

X-Ray Diffraction

Atoms, molecules, and ions are much too small to be seen with the eye. The arrangements of particles in crystalline solids are determined indirectly by X-ray diffraction (scattering). In 1912, the German physicist Max von Laue (1879–1960) showed that any crystal could serve as a three-dimensional diffraction grating for incident electromagnetic radiation with wavelengths approximating the internuclear separations of atoms in the crystal. Such radiation is in the X-ray region of the electromagnetic spectrum. Using an apparatus such as that shown in Figure 13-19, a monochromatic (single-wavelength) X-ray beam is defined by a system of slits and directed onto a crystal. The crystal is rotated to vary the angle of incidence θ . At various angles, strong beams of deflected X-rays hit a photographic plate. Upon development, the plate shows a set of symmetrically arranged spots due to deflected X-rays. Different crystals produce different arrangements of spots.

In 1913, the English scientists William (1862–1942) and Lawrence (1890–1971) Bragg found that diffraction photographs are more easily interpreted by considering the crystal as a reflection grating rather than a diffraction grating. The analysis of the spots is somewhat complicated, but an experienced crystallographer can determine the separations between atoms within identical layers and the distances between layers of atoms. The more electrons an atom has, the more strongly it scatters X-rays, so it is also possible to determine the identities of individual atoms using this technique.

Figure 13-20 illustrates the determination of spacings between layers of atoms. The X-ray beam strikes parallel layers of atoms in the crystal at an angle θ . Those rays colliding with atoms in the first layer are reflected at the same angle θ . Those passing through the first layer may be reflected from the second layer, third layer, and so forth. A reflected beam results only if all rays are in phase.

For the waves to be in phase (interact constructively), the difference in path length must be equal to the wavelength, λ , times an integer, n . This leads to the condition known as the **Bragg equation**.

$$n\lambda = 2d \sin \theta \quad \text{or} \quad \sin \theta = \frac{n\lambda}{2d}$$

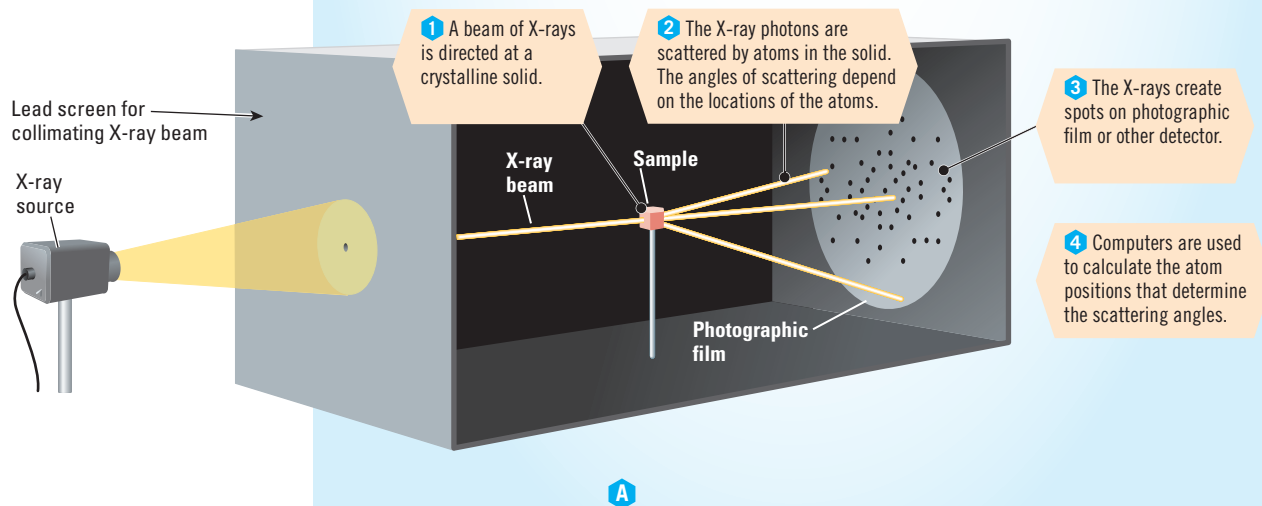
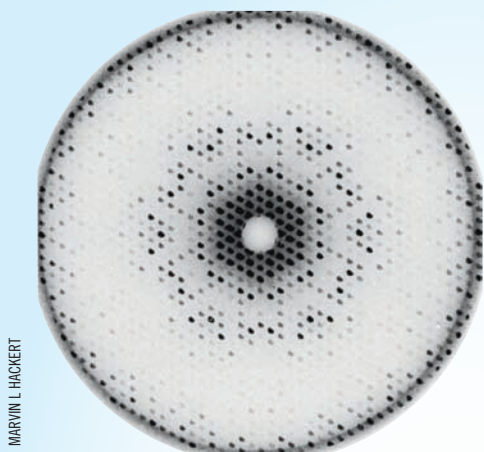


Figure 13-19 (a) X-ray diffraction by crystals (schematic).

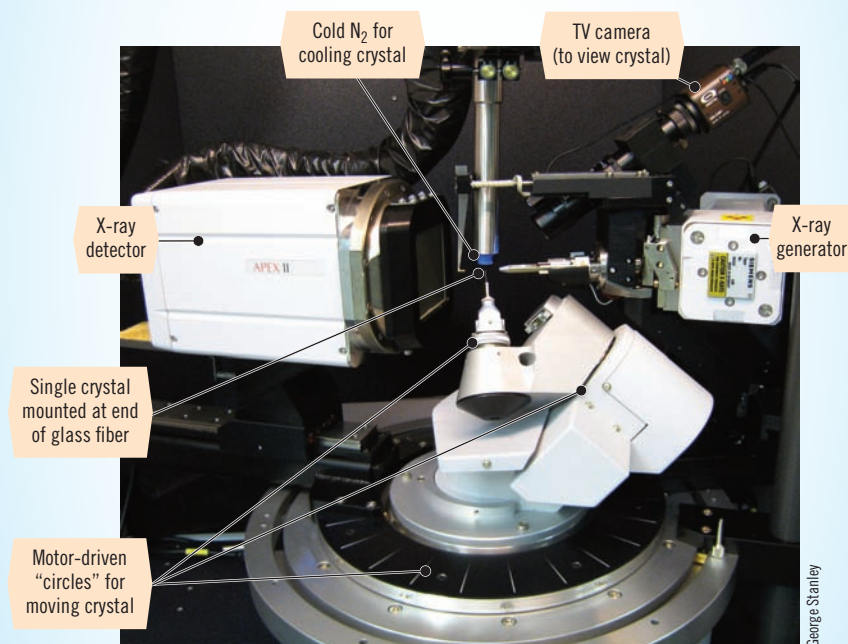
It tells us that for X-rays of a given wavelength λ , atoms in planes separated by distances d give rise to reflections at angles of incidence θ . The reflection angle increases with increasing order, $n = 1, 2, 3, \dots$



MARVIN L. HACKERT

B

Figure 13-19 (b) A photograph of the X-ray diffraction pattern from a crystal of the enzyme histidine decarboxylase (MW $\approx 37,000$ amu). The crystal was rotated so that many different lattice planes with different spacings were moved in succession into diffracting position (see Figure 13-20).



George Stanley

A modern single-crystal X-ray diffractometer system.

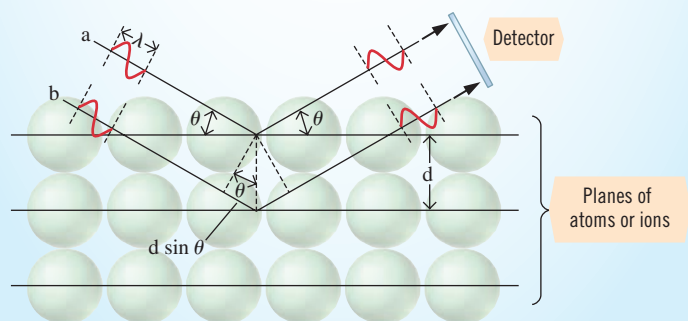
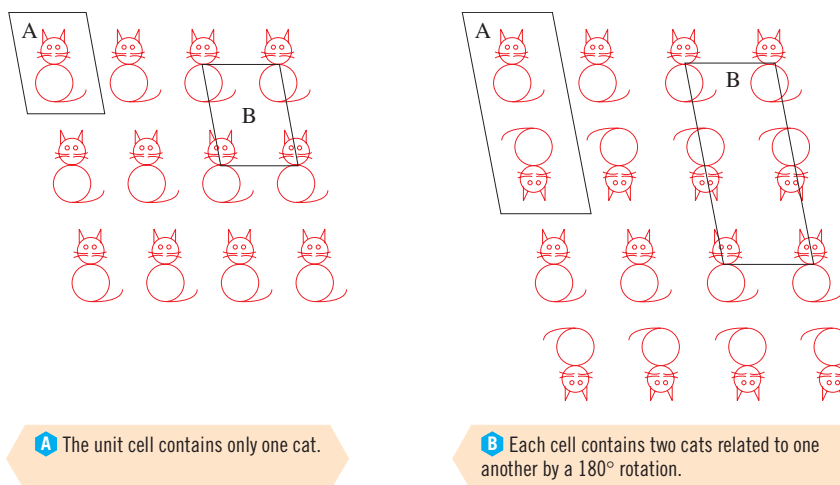


Figure 13-20 Reflection of a monochromatic beam of X-rays by two lattice planes (layers of atoms) of a crystal.

Figure 13-21 Patterns that repeat in two dimensions. Such patterns might be used to make wallpaper. We must imagine that the pattern extends indefinitely (to the end of the wall). In each pattern two of the many possible choices of unit cells are outlined. Once we identify a unit cell and its contents, repetition by translating this unit generates the entire pattern. Any crystal is an analogous pattern in which the contents of the three-dimensional unit cell consist of atoms, molecules, or ions. The pattern extends in *three* dimensions to the boundaries of the crystal, usually including many thousands of unit cells.



13-15 Structures of Crystals

All crystals contain regularly repeating arrangements of atoms, molecules, or ions. They are analogous (but in three dimensions) to a wallpaper pattern (Figure 13-21). Once we discover the pattern of a wallpaper, we can repeat it in two dimensions to cover a wall. To describe such a repeating pattern we must specify two things: (1) the size and shape of the repeating unit and (2) the contents of this unit. In the wallpaper pattern of Figure 13-21a, two different choices of the repeating unit are outlined. Repeating unit A contains one complete cat; unit B, with the same area, contains parts of four different cats, but these still add up to one complete cat. From whichever unit we choose, we can obtain the entire pattern by repeatedly translating the contents of that unit in two dimensions.

In a crystal the repeating unit is three-dimensional; its contents consist of atoms, molecules, or ions. The smallest unit of volume of a crystal that shows all the characteristics of the crystal's pattern is its **unit cell**. We note that the unit cell is just the fundamental *box* that describes the arrangement. The unit cell is described by the lengths of its edges— a , b , c (which are related to the spacings between layers, d)—and the angles between the edges— α , β , γ (Figure 13-22). Unit cells are stacked in three dimensions to build a lattice, the three-dimensional *arrangement* corresponding to the crystal. It can be proven that unit cells must fit into one of the seven crystal systems (Table 13-9). Each crystal system is distinguished by the relations between the unit cell lengths and angles *and* by the symmetry of the resulting three-dimensional patterns. Crystals have the same symmetry as their constituent unit cells because all crystals are repetitive multiples of such cells.

For a mathematical description, we can replace each repeat unit in the crystal by a point (called a *lattice point*) placed at the same place in the unit. All such points have the same environment and are indistinguishable from one another. The resulting three-dimensional array

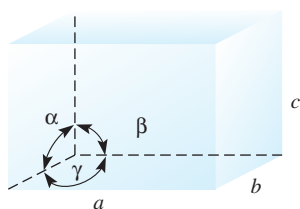


Figure 13-22 A representation of a unit cell.

Table 13-9 The Unit Cell Relationships for the Seven Crystal Systems*

System	Unit Cell		Example (common name)
	Lengths	Angles	
cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl (rock salt)
tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO ₂ (rutile)
orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	MgSO ₄ · 7H ₂ O (epsomite)
monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	CaSO ₄ · 2H ₂ O (gypsum)
triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇ (potassium dichromate)
hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	SiO ₂ (silica)
rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	CaCO ₃ (calcite)

*In these definitions, the sign $\neq$ means “is not necessarily equal to.”

Unless otherwise noted, all content on this page is © Cengage Learning.

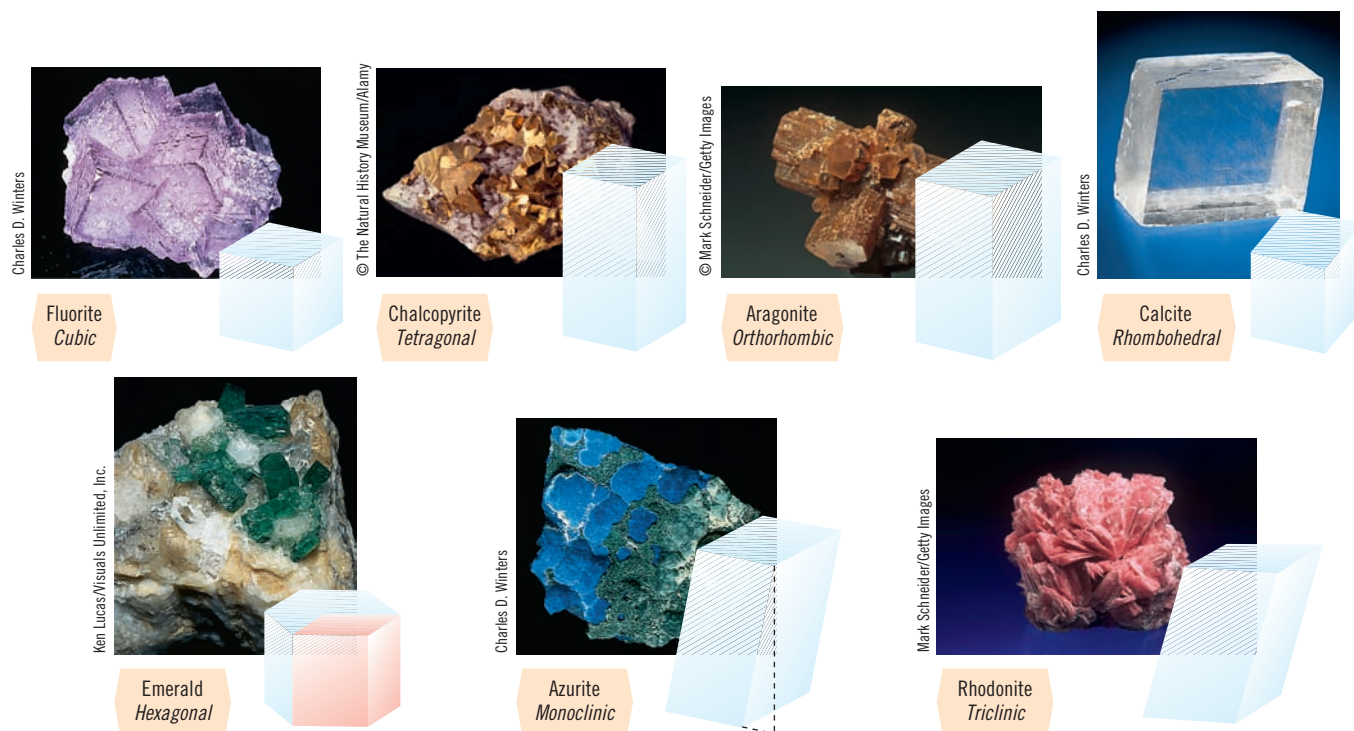


Figure 13-23 Shapes of unit cells for the seven crystal systems and a representative mineral of each system.

of points is called a *lattice*. It is a simple but complete description of the basic geometric pattern of the crystal structure.

The unit cells shown in Figure 13-23 are the simple, or primitive, unit cells corresponding to the seven crystal systems listed in Table 13-9. Each of these unit cells corresponds to *one* lattice point. As a two-dimensional representation of the reasoning behind this statement, look at the unit cell marked “B” in Figure 13-21a. Each corner of the unit cell is a lattice point, and can be imagined to represent one cat. The cat at each corner is shared among four unit cells (remember—we are working in two dimensions here). The unit cell has four corners, and in the corners of the unit cell are enough pieces to make one complete cat. Thus, unit cell B contains one cat, the same as the alternative unit cell choice marked “A.” Now imagine that each lattice point in a three-dimensional crystal represents

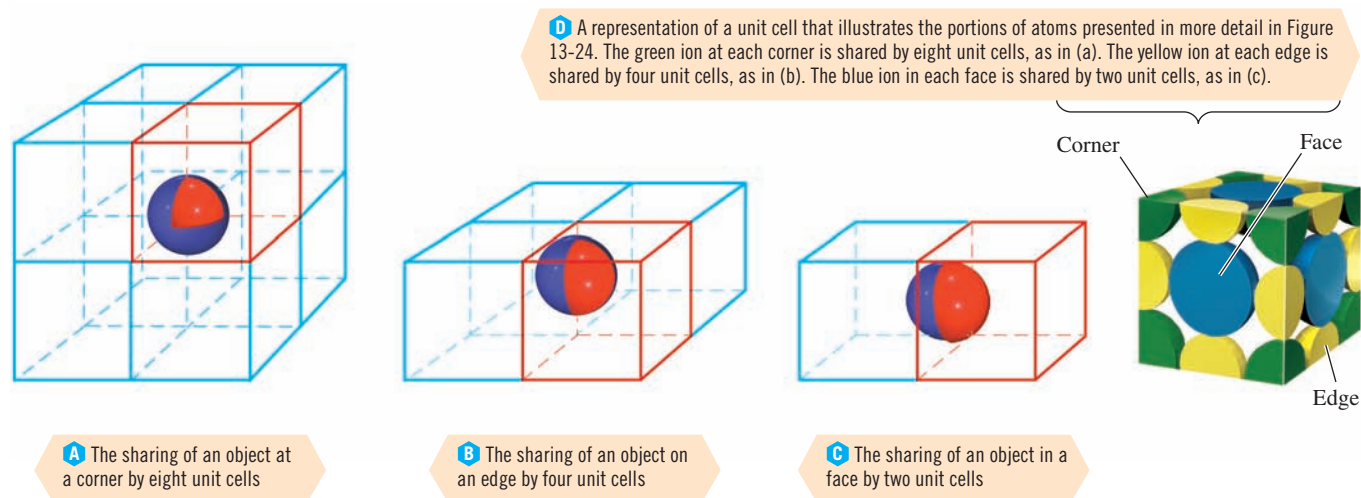


Figure 13-24 Representation of the sharing of an object (an atom, ion, or molecule) among unit cells. The fraction of each sphere that “belongs” to a single unit cell is shown in red.

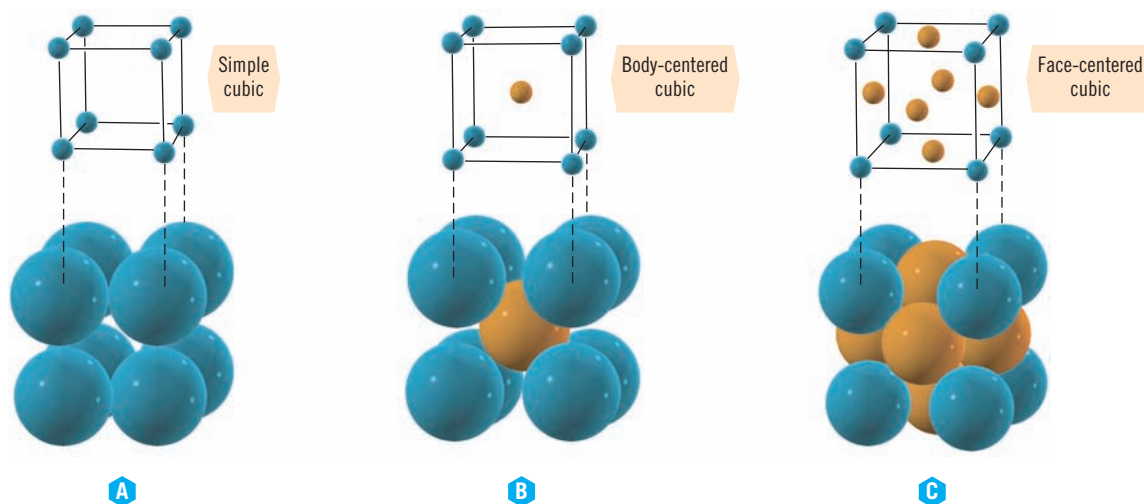


Figure 13-25 Unit cells for (a) simple cubic, (b) body-centered cubic, and (c) face-centered cubic. The spheres in each figure represent *identical* atoms or ions; different colors are shown *only* to help you visualize the spheres in the center of the cube in body-centered cubic (b) and in face-centered cubic (c) forms.

an object (a molecule, an atom, and so on). Such an object at a corner (Figure 13-24a) is shared by the eight unit cells that meet at that corner. Each unit cell has eight corners, so it contains eight “pieces” of the object, so it contains $8 \times \frac{1}{8} = 1$ object. Similarly, an object on an edge, but not at a corner, is shared by four unit cells (see Figure 13-24b), and an object on a face is shared by two unit cells (see Figure 13-24c).

Each unit cell contains atoms, molecules, or ions in a definite arrangement. Often the unit cell contents are related by some additional symmetry. (For instance, the unit cell in Figure 13-21b contains *two* cats, related to one another by a rotation of 180° .) Different substances that crystallize in the same type of lattice with the same atomic arrangement are said to be **isomorphous**. A single substance that can crystallize in more than one arrangement is said to be **polymorphous**.

In a *simple*, or *primitive*, lattice, only the eight corners of the unit cell are equivalent. In other types of crystals, objects equivalent to those forming the outline of the unit cell may occupy extra positions within the unit cell. (In this context, “equivalent” means that the same atoms, molecules, or ions appear in *identical environments and orientations* at the eight corners of the cell and, when applicable, at other locations in the unit cell.) This results in additional lattices besides the simple ones in Figure 13-23. Two of these are shown in Figure 13-25b and c. A *body-centered* lattice has equivalent points at the eight unit cell corners *and* at the center of the unit cell (see Figure 13-25). Iron, chromium, and many other metals crystallize in a body-centered cubic (bcc) arrangement. The unit cell of such a metal contains $8 \times \frac{1}{8} = 1$ atom at the corners of the cell *plus* one atom at the center of the cell (and therefore entirely in this cell); this makes a total of *two* atoms per unit cell. A *face-centered* structure involves the eight points at the corners and six more equivalent points, one in the middle of each of the six square faces of the cell. A metal (calcium and silver are cubic examples) that crystallizes in this arrangement has $8 \times \frac{1}{8} = 1$ atom at the corners *plus* $6 \times \frac{1}{2} = 3$ more in the faces, for a total of *four* atoms per unit cell. In more complicated crystals, each lattice site may represent several atoms or an entire molecule.

We have discussed some simple structures that are easy to visualize. More complex compounds crystallize in structures with unit cells that can be more difficult to describe. Experimental determination of the crystal structures of such solids is correspondingly more complex. Modern computer-controlled instrumentation can collect and analyze the large amounts of X-ray diffraction data used in such studies. This now allows analysis of structures ranging from simple metals to complex biological molecules such as proteins and nucleic acids. Most of our knowledge about the three-dimensional arrangements of atoms depends on crystal structure studies.

► A crystal of one form of polonium metal has Po atoms at the corners of a simple cubic unit cell that is $3.35 \text{ \AA}$ on edge (Example 13-8).

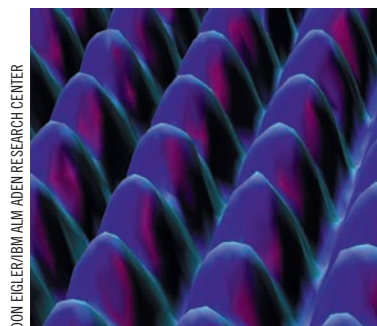
► Each object in a face is shared between two unit cells, so it is counted $\frac{1}{2}$ in each; there are six faces in each unit cell.

13-16 Bonding in Solids

We classify crystalline solids into categories according to the types of particles in the crystal and the bonding or interactions among them. The four categories are (1) metallic solids, (2) ionic solids, (3) molecular solids, and (4) covalent solids. Table 13-10 summarizes these categories of solids and their typical properties.

Metallic Solids

Metals crystallize as solids in which metal ions may be thought to occupy the lattice sites and are embedded in a cloud of delocalized valence electrons. Nearly all metals crystallize in one of three types of lattices: (1) body-centered cubic (bcc), (2) face-centered cubic (fcc; also called cubic close-packed), and (3) hexagonal close-packed. The latter two types are called close-packed structures because the particles (in this case metal atoms) are packed together as closely as possible. The differences between the two close-packed structures are illustrated in Figures 13-26 and 13-27. Let spheres of equal size represent identical metal atoms, or any other particles, that form close-packed structures. Consider a layer of spheres packed in a plane, *A*, as closely as possible (Figure 13-27a). An identical plane of spheres, *B*, is placed in the depressions of plane *A*. If the third plane is placed with its spheres directly above those in plane *A*, the *ABA* arrangement results. This is the hexagonal close-packed structure (see Figure 13-27a). The extended pattern of arrangement of planes is *ABABAB*.... If the third layer is placed in the alternate set of depressions in the

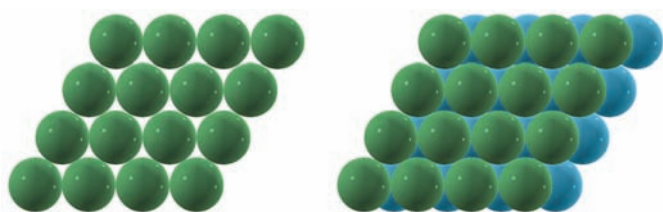


Scanning tunneling microscope image of nickel atoms on the surface of nickel metal.

Table 13-10 Characteristics of Types of Solids

	Metallic	Ionic	Molecular	Covalent
Particles of unit cell	Metal ions in “electron cloud”	Anions, cations	Molecules (or atoms)	Atoms
Strongest interparticle forces	Metallic bonds (due to attraction between cations and e^- 's)	Electrostatic	Dispersion, dipole–dipole, and/or hydrogen bonds	Covalent bonds
Properties	Soft to very hard; good thermal and electrical conductors; wide range of melting points (–39 to 3400°C)	Hard; brittle; poor thermal and electrical conductors; high melting points (400 to 3000°C)	Soft; poor thermal and electrical conductors; low melting points (–272 to 400°C)	Very hard; poor thermal and electrical conductors;* high melting points (1200 to 4000°C)
Examples	Li, K, Ca, Cu, Cr, Ni (metals)	NaCl, CaBr ₂ , K ₂ SO ₄ (typical salts)	CH ₄ (methane), P ₄ , O ₂ , Ar, CO ₂ , H ₂ O, S ₈	C (diamond), SiO ₂ (quartz)

*Exceptions: Diamond is a good conductor of heat; graphite is soft and conducts electricity well.



A Spheres in the same plane, packed as closely as possible. Each sphere touches six others.

B Spheres in two planes, packed as closely as possible. All spheres represent *identical* atoms or ions; different colors are shown *only* to help you visualize the layers. Real crystals have many more than two planes. Each sphere touches six others in its own layer, three in the layer below it, and three in the layer above it; that is, it contacts a total of 12 other spheres (has a coordination number of 12).

Figure 13-26

► The **coordination number** of a molecule or ion is its number of nearest neighbors in a crystal. This term is used differently in discussions of coordination chemistry (see Section 25-3).

second layer so that spheres in the first and third layers are not directly above and below each other, the cubic close-packed structure, $ABCABCABC \dots$, results (see Figure 13-27b). In close-packed structures each sphere has a *coordination number* of 12, that is, 12 nearest neighbors. In ideal close-packed structures 74% of a given volume is due to spheres and 26% is empty space. The body-centered cubic structure is less efficient in packing; each sphere has only eight nearest neighbors, and there is more empty space.

► The most efficient solid-state packing is usually preferred in order to minimize the amount of “empty” space in a structure. The exact crystal structure type, however, can vary depending on the shapes and sizes of the ions, atoms, or molecules making up the solid.

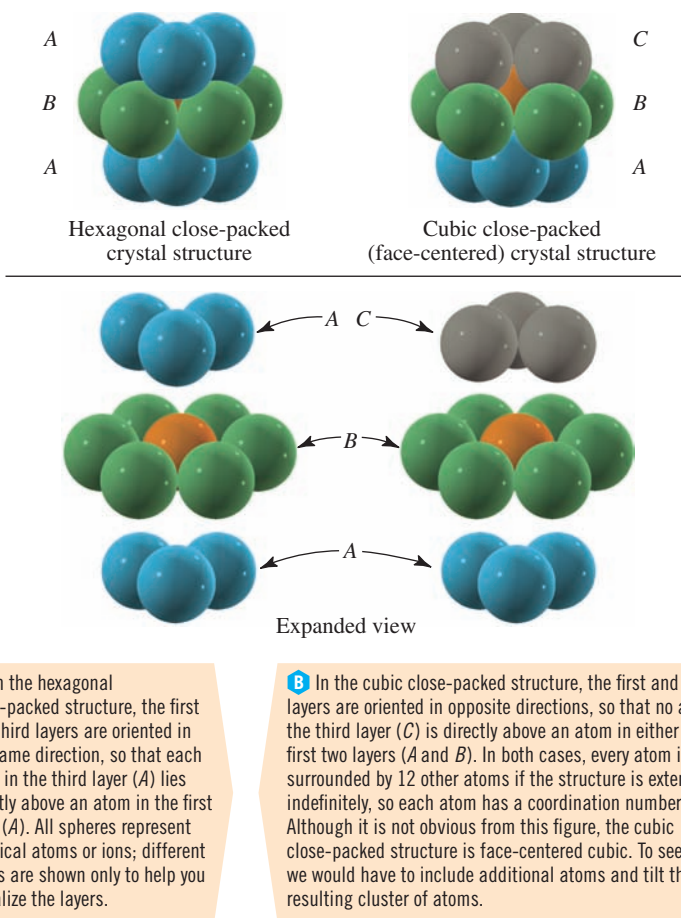
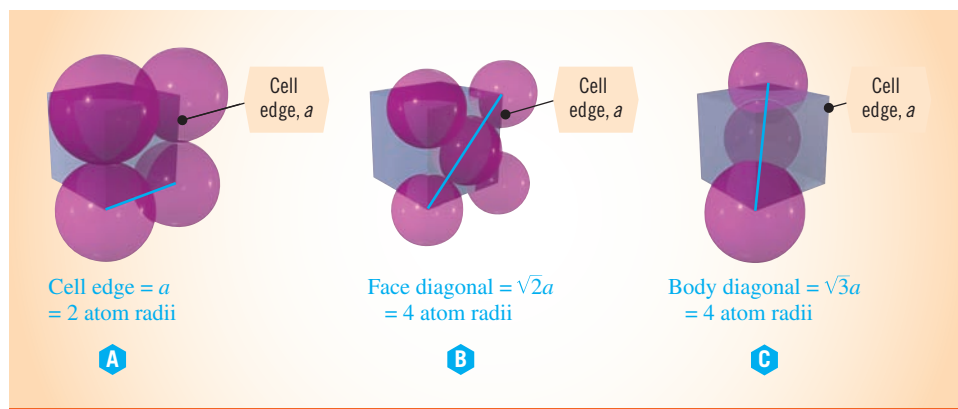


Figure 13-27 There are two crystal structures in which atoms are packed together as compactly as possible. The diagrams show the structures expanded to clarify the difference between them.

Problem-Solving Tip The Locations of the Nearest Neighbors in Cubic Crystals

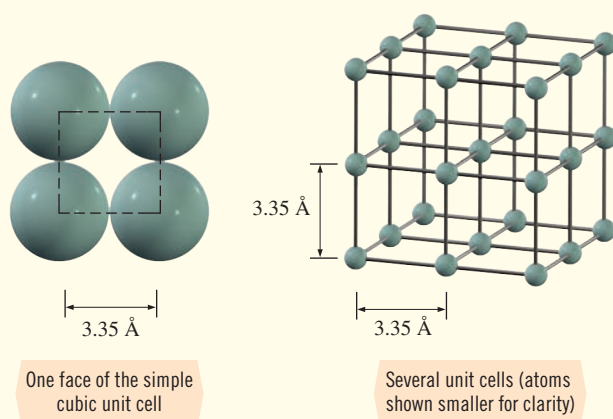
The distance from an atom to one of its nearest neighbors in any crystal structure depends on the arrangement of atoms and on the size of the unit cell. For structures (such as metals) that contain only one kind of atom, the nearest neighbors of each atom can be visualized as follows. (Recall that for a cubic structure, the unit cell edge is a .) In a simple cubic structure, the nearest neighbors are along the cell edge (a). In a face-centered cubic structure, the nearest neighbors are along the face diagonal (b). In a body-centered cubic structure, they are along the body diagonal (c). The relationships just described hold only for structures composed of a single kind of atom. For other structures, the relationships are more complex.

**EXAMPLE 13-8 Nearest Neighbors**

In the simple cubic form of polonium there are Po atoms at the corners of a simple cubic unit cell that is $3.35 \text{ \AA}$ on edge. (a) What is the shortest distance between centers of neighboring Po atoms? (b) How many nearest neighbors does each atom have?

Plan

We visualize the simple cubic cell.

**Solution**

- One face of the cubic unit cell is shown in the left-hand drawing, with the atoms touching. The centers of the nearest neighbor atoms are separated by one unit cell edge, at the distance $3.35 \text{ \AA}$.
- A three-dimensional representation of eight unit cells is also shown. In that drawing the atoms are shown smaller for clarity. Consider the atom at the intersection of the eight unit cells. As we can see, this atom has **six nearest neighbors**, one in each of the unit cell directions. The same would be true of any atom in the structure.

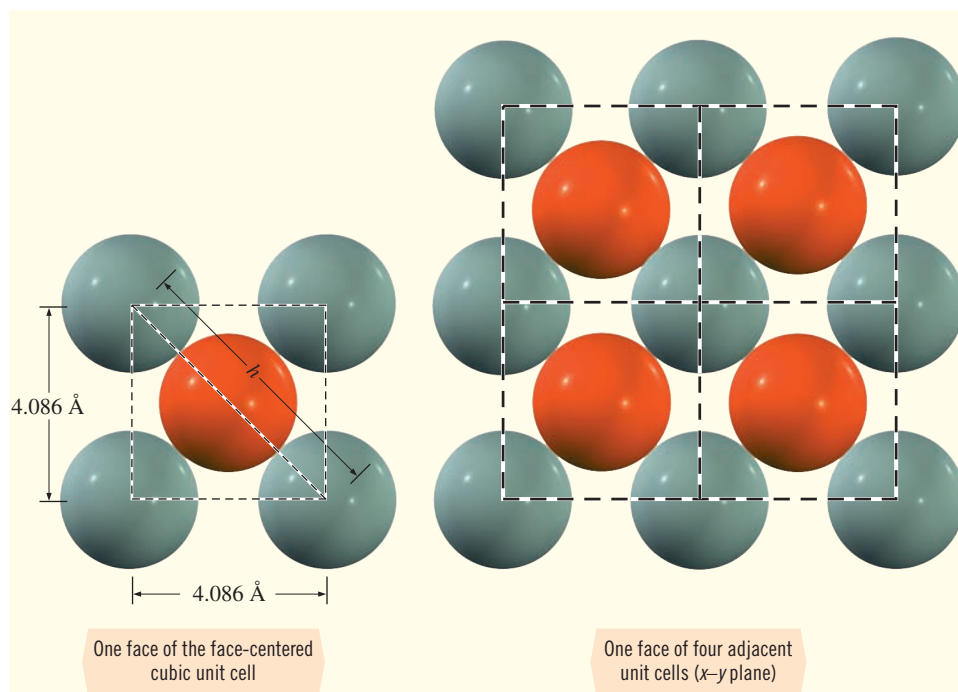
EXAMPLE 13-9 Nearest Neighbors

Silver crystals are face-centered cubic, with a cell edge of $4.086 \text{ \AA}$. (a) What is the distance between centers of the two closest Ag atoms? (b) What is the atomic radius of silver in this crystal? (c) How many nearest neighbors does each atom have?

Plan

We reason as in Example 13-8, except that now the two atoms closest to each other are those along the face diagonal.

► In this figure, all atoms are identical; different colors are shown only to help clarify the explanation.



Solution

- (a) One face of the face-centered cubic unit cell is shown in the left-hand drawing, with the atoms touching. The nearest neighbor atoms are the ones along the diagonal of the face of the cube. We may visualize the face as consisting of two right isosceles triangles sharing a common hypotenuse, h , and having sides of length $a = 4.086 \text{ Å}$. The hypotenuse is equal to *twice* the center-to-center distance. The hypotenuse can be calculated from the Pythagorean theorem, $h^2 = a^2 + a^2$. The length of the hypotenuse equals the square root of the sum of the squares of the sides.

$$h = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2(4.086\text{Å})^2} = 5.778 \text{ Å}$$

The distance between centers of adjacent silver atoms is one half of h , so

$$\text{Distance} = \frac{5.778 \text{ Å}}{2} = 2.889 \text{ Å}$$

- (b) The hypotenuse of the unit cell face is four times the radius of the silver atom.

$$\text{Atom radius} = \frac{5.778 \text{ Å}}{4} = 1.444 \text{ Å}$$

- (c) To see the number of nearest neighbors, we expand the left-hand drawing to include several unit cells, as shown in the right-hand drawing. Suppose that this is the x - y plane. The atom shown in orange has four nearest neighbors in this plane. There are four more such neighbors in the x - z plane (perpendicular to the x - y plane), and four additional neighbors in the y - z plane (also perpendicular to the x - y plane). This gives a total of **12 nearest neighbors** (coordination number 12).

EXAMPLE 13-10 Density and Cell Volume

From data in Example 13-9, calculate the density of metallic silver.

Plan

We first determine the mass of a unit cell, that is, the mass of four atoms of silver. The density of the unit cell, and therefore of silver, is its mass divided by its volume.

Solution

$$\begin{aligned}\underline{?} \text{ g Ag per unit cell} &= \frac{4 \text{ Ag atoms}}{\text{unit cell}} \times \frac{1 \text{ mol Ag}}{6.022 \times 10^{23} \text{ Ag atoms}} \times \frac{107.87 \text{ g Ag}}{1 \text{ mol Ag}} \\ &= 7.165 \times 10^{-22} \text{ g Ag/unit cell}\end{aligned}$$

$$V_{\text{unit cell}} = (4.086 \text{ \AA})^3 = 68.22 \text{ \AA}^3 \times \left(\frac{10^{-8} \text{ cm}}{\text{\AA}}\right)^3 = 6.822 \times 10^{-23} \text{ cm}^3/\text{unit cell}$$

$$\text{Density} = \frac{7.165 \times 10^{-22} \text{ g Ag/unit cell}}{6.822 \times 10^{-23} \text{ cm}^3/\text{unit cell}} = 10.50 \text{ g/cm}^3$$

► A handbook gives the density of silver as 10.5 g/cm³ at 20°C.

You should now work Exercises 90 and 92.

Data obtained from crystal structures and observed densities give us information from which we can calculate the value of Avogadro's number. The next example illustrates these calculations.

EXAMPLE 13-11 Density, Cell Volume, and Avogadro's Number

Titanium crystallizes in a body-centered cubic unit cell with an edge length of 3.306 Å. The density of titanium is 4.401 g/cm³. Use these data to calculate Avogadro's number.

Plan

We relate the density and the volume of the unit cell to find the total mass contained in one unit cell. Knowing the number of atoms per unit cell, we can then find the mass of one atom. Comparing this to the known atomic weight, which is the mass of one mole (Avogadro's number) of atoms, we can evaluate Avogadro's number.

Solution

We first determine the volume of the unit cell.

$$V_{\text{cell}} = (3.306 \text{ \AA})^3 = 36.13 \text{ \AA}^3$$

We now convert Å³ to cm³.

$$\underline{?} \text{ cm}^3 = 36.13 \text{ \AA}^3 \times \left(\frac{10^{-8} \text{ cm}}{\text{\AA}}\right)^3 = 3.613 \times 10^{-23} \text{ cm}^3$$

The mass of the unit cell is its volume times the observed density.

$$\text{Mass of unit cell} = 3.613 \times 10^{-23} \text{ cm}^3 \times \frac{4.401 \text{ g}}{\text{cm}^3} = 1.590 \times 10^{-22} \text{ g}$$

The bcc unit cell contains $8 \times \frac{1}{8} + 1 = 2$ Ti atoms, so this represents the mass of two Ti atoms. The mass of a single Ti atom is

$$\text{Mass of atom} = \frac{1.590 \times 10^{-22} \text{ g}}{2 \text{ atoms}} = 7.950 \times 10^{-23} \text{ g/atom}$$

From the known atomic weight of Ti (47.88), we know that the mass of one mole of Ti is 47.88 g/mol. Avogadro's number represents the number of atoms per mole, and can be calculated as

$$N_{\text{Av}} = \frac{47.88 \text{ g}}{\text{mol}} \times \frac{1 \text{ atom}}{7.950 \times 10^{-23} \text{ g}} = 6.023 \times 10^{23} \text{ atoms/mol}$$

You should now work Exercise 96.

Ionic Solids

Most salts crystallize as ionic solids with ions occupying the unit cell. Sodium chloride (Figure 13-28) is an example. Many other salts crystallize in the sodium chloride (face-centered cubic) arrangement. Examples are the halides of Li^+ , K^+ , and Rb^+ , and $\text{M}^{2+}\text{X}^{2-}$ oxides and sulfides such as MgO , CaO , CaS , and MnO . Two other common ionic structures are those of cesium chloride, CsCl (simple cubic lattice), and zincblende, ZnS (face-centered cubic lattice), shown in Figure 13-29. Salts that are isomorphous with the CsCl structure include CsBr , CsI , NH_4Cl , TlCl , TlBr , and TlI . The sulfides of Be^{2+} , Cd^{2+} , and Hg^{2+} , together with CuBr , CuI , AgI , and ZnO , are isomorphous with the zincblende structure (see Figure 13-29c).

Ionic solids are usually poor electrical and thermal conductors. Liquid (molten) ionic compounds are excellent electrical conductors, however, because their ions are freely mobile.

In certain types of solids, including ionic crystals, particles *different* from those at the corners of the unit cell occupy extra positions within the unit cell. For example, the face-centered cubic unit cell of sodium chloride can be visualized as having chloride ions at the corners and middles of the faces; sodium ions are on the edges between the chloride ions and in the center (see Figures 13-28 and 13-29b). Thus, a unit cell of NaCl contains the following.

$$\text{Cl}^- \left(\begin{array}{l} \text{eight at} \\ \text{corners} \\ (8 \times \frac{1}{8}) \end{array} \right) + \left(\begin{array}{l} \text{six in middles} \\ \text{of faces} \\ (6 \times \frac{1}{2}) \end{array} \right) = 1 + 3 = 4 \text{ Cl}^- \text{ ions/unit cell}$$

$$\text{Na}^+ \left(\begin{array}{l} \text{twelve on} \\ \text{edges} \\ (12 \times \frac{1}{4}) \end{array} \right) + \left(\begin{array}{l} \text{one in} \\ \text{center} \\ (1) \end{array} \right) = 3 + 1 = 4 \text{ Na}^+ \text{ ions/unit cell}$$

The unit cell contains equal numbers of Na^+ and Cl^- ions, as required by its chemical formula. Alternatively, we could translate the unit cell by half its length in any axial direc-

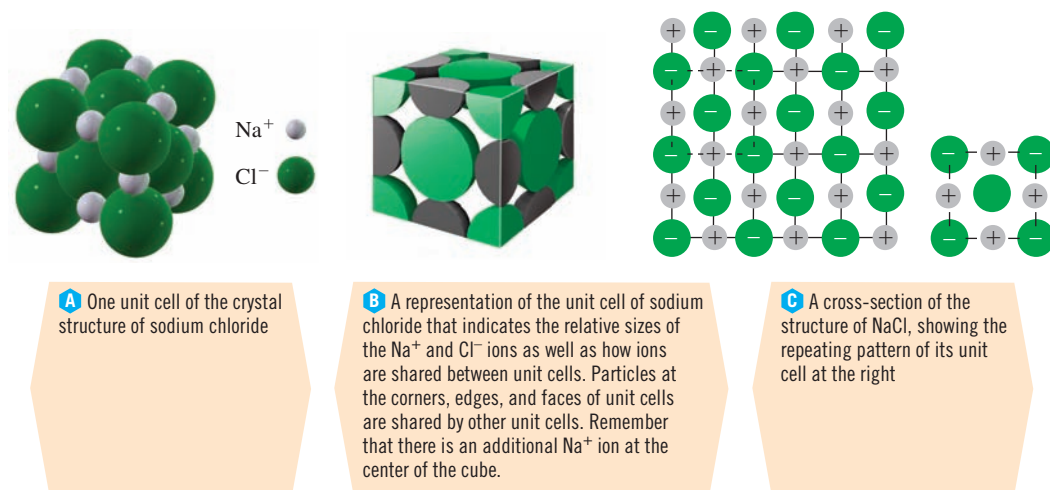


Figure 13-28 Some representations of the crystal structure of sodium chloride, NaCl . Sodium ions are shown in gray and chloride ions are shown in green.

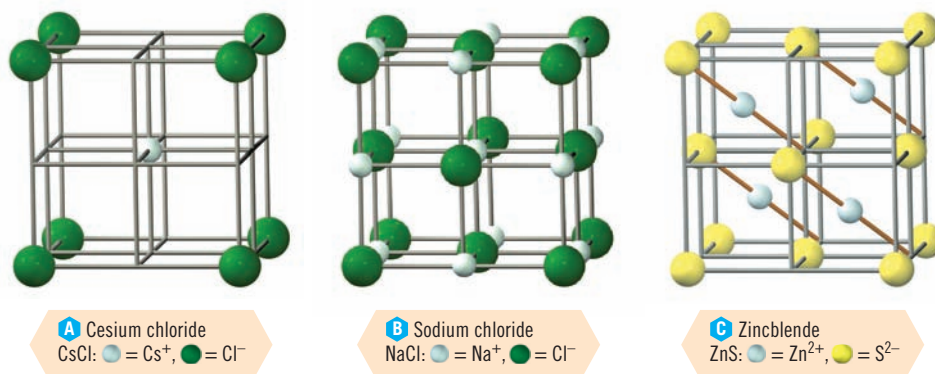


Figure 13-29 Crystal structures of some ionic compounds of the MX type. The gray circles represent cations. One unit cell of each structure is shown. (a) The structure of cesium chloride, CsCl, is simple cubic. It is *not* body-centered, because the point at the center of the cell (Cs^+ , gray) is not the same as the point at a corner of the cell (Cl^- , green). (b) Sodium chloride, NaCl, is face-centered cubic. (c) Zincblende, ZnS, is face-centered cubic, with four Zn^{2+} (gray) and four S^{2-} (yellow) ions per unit cell. The Zn^{2+} ions are related by the same translations as the S^{2-} ions.

tion within the lattice and visualize the unit cell in which sodium and chloride ions have exchanged positions. Such an exchange is not always possible. You should confirm that this alternative description also gives four chloride ions and four sodium ions per unit cell.

Ionic radii such as those in Figure 5-4 and Table 14-1 are obtained from X-ray crystallographic determinations of unit cell dimensions, assuming that adjacent ions are in contact with each other.

EXAMPLE 13-12 Ionic Radii from Crystal Data

Lithium bromide, LiBr, crystallizes in the NaCl face-centered cubic structure with a unit cell edge length of $a = b = c = 5.501 \text{ \AA}$. Assume that the Br^- ions at the corners of the unit cell are in contact with those at the centers of the faces. Determine the ionic radius of the Br^- ion. One face of the unit cell is depicted in Figure 13-30.

Plan

We may visualize the face as consisting of two right isosceles triangles sharing a common hypotenuse, h , and having sides of length $a = 5.501 \text{ \AA}$. The hypotenuse is equal to four times the radius of the bromide ion, $h = 4r_{\text{Br}^-}$.

Solution

The hypotenuse can be calculated from the Pythagorean theorem, $h^2 = a^2 + a^2$. The length of the hypotenuse equals the square root of the sum of the squares of the sides.

$$h = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2(5.501 \text{ \AA})^2} = 7.780 \text{ \AA}$$

The radius of the bromide ion is one fourth of h , so

$$r_{\text{Br}^-} = \frac{7.780}{4} = 1.945 \text{ \AA}$$

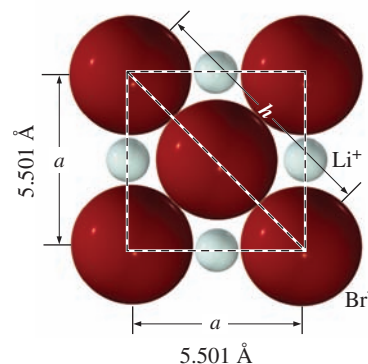


Figure 13-30 One face of the face-centered cubic unit cell of lithium bromide (Example 13-12).

EXAMPLE 13-13 Ionic Radii from Crystal Data

Refer to Example 13-12. Calculate the ionic radius of Li^+ in LiBr, assuming anion–cation contact along an edge of the unit cell.

Plan

The edge length, $a = 5.501 \text{ \AA}$, is twice the radius of the Br^- ion plus twice the radius of the Li^+ ion. We know from Example 13-12 that the radius for the Br^- ion is $1.945 \text{ \AA}$.

Solution

$$5.501 \text{ \AA} = 2r_{\text{Br}^-} + 2r_{\text{Li}^+}$$

$$2r_{\text{Li}^+} = 5.501 \text{ \AA} - 2(1.945 \text{ \AA}) = 1.611 \text{ \AA}$$

$$r_{\text{Li}^+} = 0.806 \text{ \AA}$$

You should now work Exercise 88.

The value of $1.945 \text{ \AA}$ for the Br^- radius calculated in Example 13-12 is somewhat different from the value of $1.82 \text{ \AA}$ given in Figure 5-4; the Li^+ value of $0.806 \text{ \AA}$ from Example 13-13 also differs somewhat from the value of $0.90 \text{ \AA}$ given in Figure 5-4. We should remember that the tabulated value in Figure 5-4 is the *average* value obtained from a number of crystal structures of compounds containing the specified ion. Calculations of ionic radii usually assume that anion–anion contact exists, but this assumption is not always true. Calculated radii therefore vary from structure to structure, and we should not place too much emphasis on a value of an ionic radius obtained from any *single* structure determination. We now see that there is some difficulty in determining precise values of ionic radii. Similar difficulties can arise in the determination of atomic radii from molecular and covalent solids or of metallic radii from solid metals.

Molecular Solids

The lattice positions that describe unit cells of molecular solids represent molecules or monatomic elements (sometimes referred to as monatomic molecules). Figure 13-31 shows the unit cells of two simple molecular crystals. Although the bonds *within* molecules are covalent and strong, the forces of attraction *between* molecules are much weaker. They range from hydrogen bonds and weaker dipole–dipole interactions in polar molecules such as H_2O and SO_2 to very weak dispersion forces in symmetrical, nonpolar molecules such as CH_4 , CO_2 , and O_2 and monatomic elements, such as the noble gases. Because of the relatively weak intermolecular forces of attraction, molecules can be easily displaced. Thus, molecular solids are usually soft substances with low melting points. Because electrons do not move from one molecule to another under ordinary conditions, molecular solids are poor electrical conductors and good insulators.

► Dispersion forces are also present among polar molecules.

Covalent Solids

Covalent solids (or “network solids”) can be considered giant molecules that consist of covalently bonded atoms in an extended, rigid crystalline network. Diamond (one crystalline

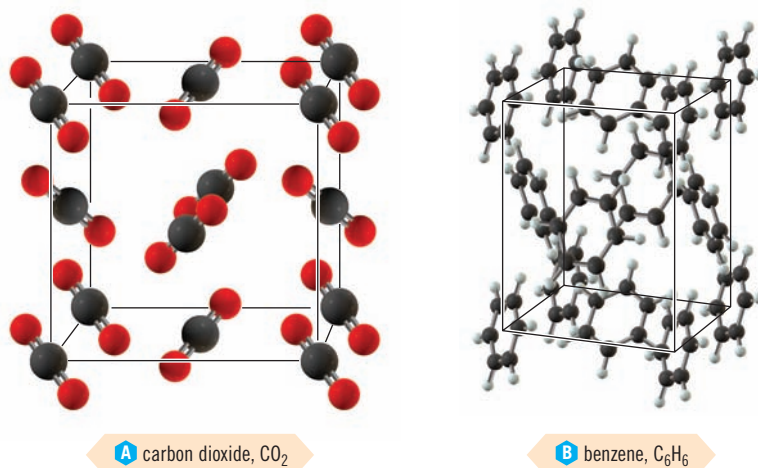


Figure 13-31 The packing arrangement in a molecular crystal depends on the shape of the molecule as well as on the electrostatic interactions of any regions of excess positive and negative charge in the molecules. The arrangements in some molecular crystals are shown here: (a) carbon dioxide, CO_2 ; (b) benzene, C_6H_6 .

Unless otherwise noted, all content on this page is © Cengage Learning.

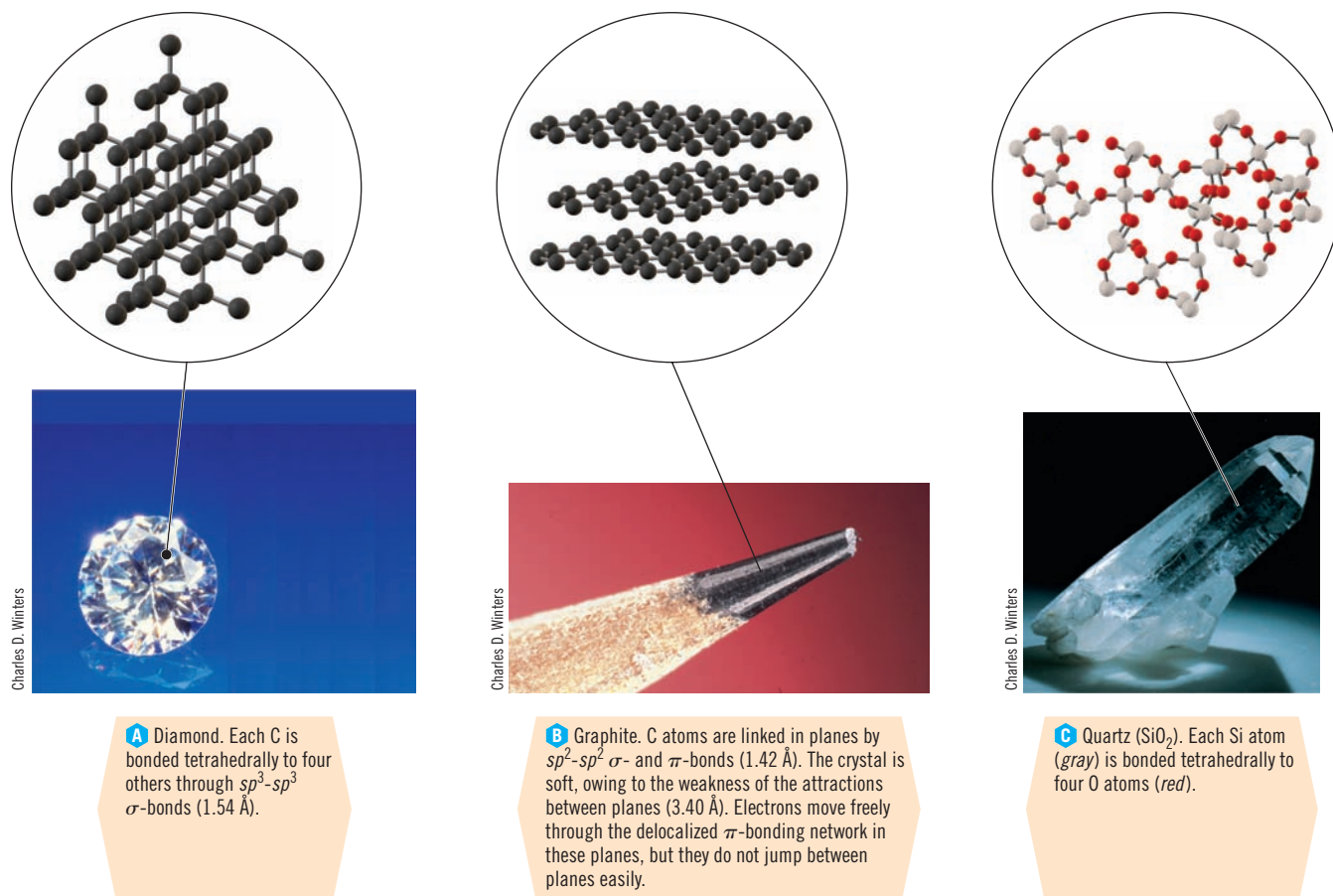


Figure 13-32 Portions of the atomic arrangements in three covalent solids.

form of carbon) and quartz are examples of covalent solids (Figure 13-32). Because of their rigid, strongly bonded structures, *most* covalent solids are very hard and melt at high temperatures. Because electrons are localized in covalent bonds, they are not freely mobile. As a result, covalent solids are *usually* poor thermal and electrical conductors at ordinary temperatures. (Diamond, however, is a good conductor of heat; jewelers use this property to distinguish gem diamonds from imitations.)

An important exception to these generalizations about properties is *graphite*, an allotropic form of carbon. It has the layer structure shown in Figure 13-32b. The overlap of an extended π -electron network in each plane makes graphite an excellent conductor. The very weak attraction between layers allows these layers to slide over one another easily. Graphite is used as a lubricant, as an additive for motor oil, and in pencil “lead” (combined with clay and other fillers to control hardness).

► It is interesting to note that these two allotropes of carbon include one very hard substance and one very soft substance. They differ only in the arrangement and bonding of the C atoms.

13-17 Band Theory of Metals

As described in the previous section, most metals crystallize in close-packed structures. The ability of metals to conduct electricity and heat must result from strong electronic interactions of an atom with its 8 to 12 nearest neighbors. This might be surprising at first if we recall that each Group 1A and Group 2A metal atom has only one or two valence electrons available for bonding. This is too few to participate in bonds localized between it and each of its nearest neighbors.

Bonding in metals is called **metallic bonding**. It results from the electrical attractions among positively charged metal ions and mobile, delocalized electrons belonging to the crystal as a whole. The properties associated with metals—metallic luster, high thermal

Unless otherwise noted, all content on this page is © Cengage Learning.

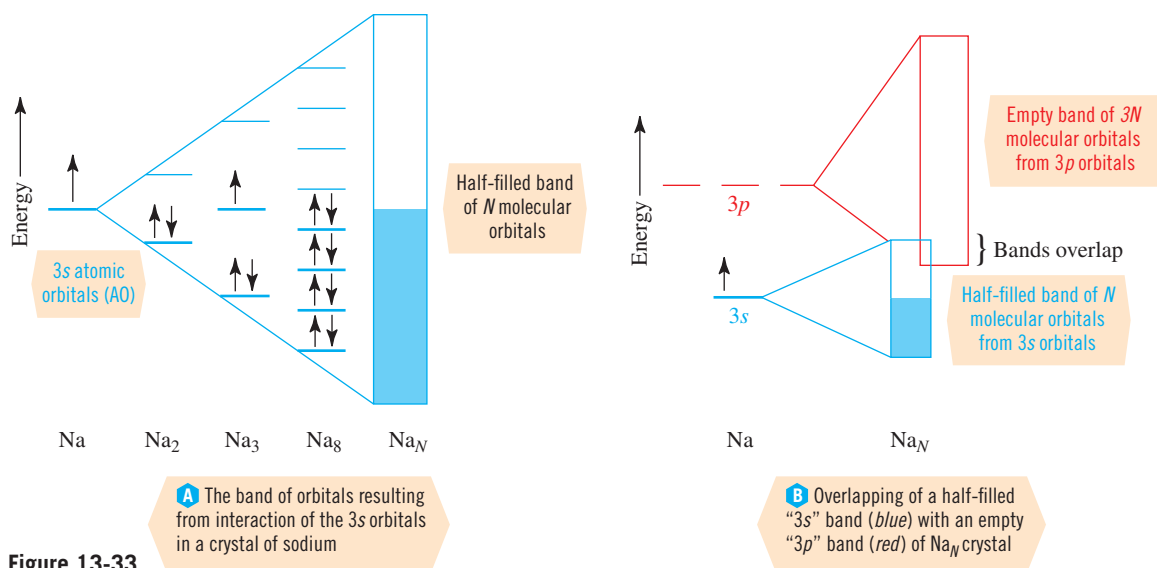
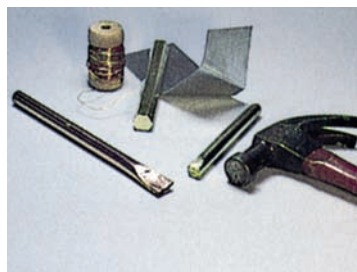


Figure 13-33



Metals can be formed into many shapes because of their malleability and ductility.

► The alkali metals are those of Group 1A; the alkaline earth metals are those of Group 2A.

and electrical conductivity, and so on—can be explained by the **band theory** of metals, which we now describe.

The overlap interaction of two atomic orbitals, say the 3s orbitals of two sodium atoms, produces two molecular orbitals, one bonding orbital and one antibonding orbital (see Chapter 9). If N atomic orbitals interact, N molecular orbitals are formed. In a single metallic crystal containing one mole of sodium atoms, for example, the interaction (overlap) of 6.022×10^{23} 3s atomic orbitals produces 6.022×10^{23} molecular orbitals. Atoms interact more strongly with nearby atoms than with those farther away. The energy that separates bonding and antibonding molecular orbitals resulting from two given atomic orbitals decreases as the overlap between the atomic orbitals decreases (see Chapter 9). The interactions among the mole of Na atoms result in a series of very closely spaced molecular orbitals (formally σ_{3s} and σ_{3s}^*). These constitute a nearly continuous **band** of orbitals that belongs to the crystal as a whole. One mole of Na atoms contributes 6.022×10^{23} valence electrons (Figure 13-33a), so the 6.022×10^{23} orbitals in the band are half-filled.

The ability of metallic Na to conduct electricity is due to the ability of any of the highest energy electrons in the “3s” band to jump to a slightly higher-energy vacant orbital in the same band when an electric field is applied. The resulting net flow of electrons through the crystal is in the direction of the applied field.

The empty 3p atomic orbitals of the Na atoms also interact to form a wide band of $3 \times 6.022 \times 10^{23}$ orbitals. The 3s and 3p atomic orbitals are quite close in energy, so the fanned-out bands of molecular orbitals overlap, as shown in Figure 13-33b. The two overlapping bands contain $4 \times 6.022 \times 10^{23}$ orbitals and only 6.022×10^{23} electrons. Because each orbital can hold two electrons, the resulting combination of 3s and 3p bands is only one-eighth full.

Overlap of “3s” and “3p” bands is not necessary to explain the ability of Na or of any other Group 1A metal to conduct electricity, as the half-filled “3s” band is sufficient for this. In the Group 2A metals, however, such overlap is important. Consider a crystal of magnesium as an example. The 3s atomic orbital of an isolated Mg atom is filled with two electrons. Thus, without this overlap, the “3s” band in a crystal of Mg is also filled. Mg is a good conductor at room temperature because the highest energy electrons are able to move readily into vacant orbitals in the “3p” band (Figure 13-34).

According to band theory, the highest-energy electrons of metallic crystals occupy either a partially filled band or a filled band that overlaps an empty band. A band within which (or into which) electrons move to allow electrical conduction is called a **conduction band**. The electrical conductivity of a metal decreases as temperature increases. The increase in temperature causes thermal agitation of the metal ions. This impedes the flow of electrons when an electric field is applied.

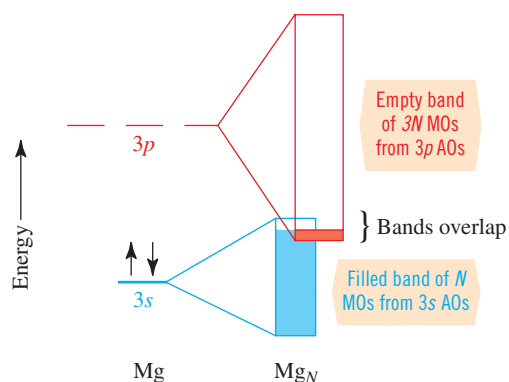


Figure 13-34 Overlapping of a filled “3s” band (blue) with an empty “3p” band of Mg_N crystal. The higher-energy electrons are able to move into the “3p” band (red) as a result of this overlap. There are now empty orbitals immediately above the filled orbitals, leading to conductivity.

Crystalline nonmetals, such as diamond and phosphorus, are **insulators**—they do not conduct electricity. The reason for this is that their highest energy electrons occupy filled bands of molecular orbitals that are separated from the lowest empty band (conduction band) by an energy difference called the **band gap** (E_g). In an insulator, this band gap is an energy difference that is too large for electrons to jump to get to the conduction band (Figure 13-35). Many ionic solids are also insulators, but are good conductors in their molten (liquid) state.

Elements that are **semiconductors** have filled bands that are only slightly below, but do not overlap with, empty bands. They do not conduct electricity at low temperatures, but a small increase in temperature is sufficient to excite some of the highest-energy electrons into the empty conduction band.

Let us now summarize some of the physical properties of metals in terms of the band theory of metallic bonding.

1. We have just accounted for the *ability of metals to conduct electricity*.
2. Metals are also *conductors of heat*. They can absorb heat as electrons become thermally excited to low-lying vacant orbitals in a conduction band. The reverse process accompanies the release of heat.
3. Metals have a *lustrous appearance* because the mobile electrons can absorb a wide range of wavelengths of radiant energy as they jump to higher energy levels. Then they emit photons of visible light and fall back to lower levels within the conduction band.
4. Metals are *malleable or ductile* (or both). A crystal of a metal is easily deformed when a mechanical stress is applied to it. All of the metal ions are identical, and they are imbedded in a “sea of electrons.” As bonds are broken, new ones are readily formed with adjacent metal ions. The features of the arrangement remain unchanged, and the environment of each metal ion is the same as before the deformation occurred (Figure 13-36). The breakage of bonds involves the promotion of electrons to higher-energy levels. The formation of bonds is accompanied by the return of the electrons to the original energy levels.



Various samples of elemental silicon. The circle at the lower right is a disk of ultrapure silicon on which many electronic circuits have been etched.

► A *malleable* substance can be rolled or pounded into sheets. A *ductile* substance can be drawn into wires. Gold is the most malleable metal known.

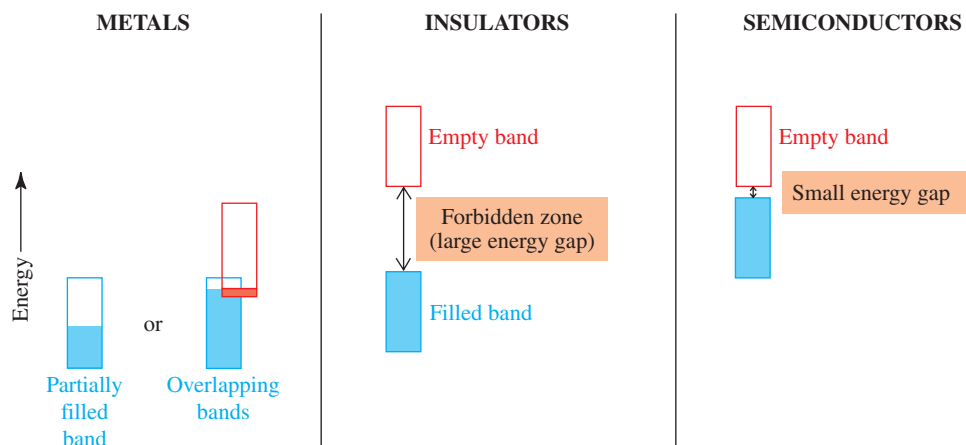


Figure 13-35 Distinction among metals, insulators, and semiconductors. In each case an unshaded area represents a conduction band.

Unless otherwise noted, all content on this page is © Cengage Learning.

CHEMISTRY IN USE

Semiconductors

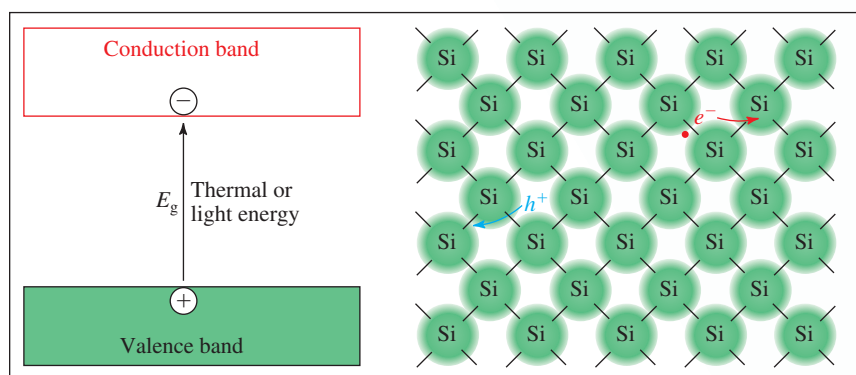
A **semiconductor** is an element or a compound with filled bands that are only slightly below, but do not overlap with, empty bands. The difference between an insulator and a semiconductor is only the size of the energy gap, and there is no sharp distinction between them. An *intrinsic* semiconductor (i.e., a semiconductor in its pure form) is a much poorer conductor of electricity than a metal because, for conduction to occur in a semiconductor, electrons must be excited from bonding orbitals in the filled *valence band* into the empty *conduction band*. Figure (a) shows how this happens. An electron that is given an excitation energy greater than or equal to the **band gap** (E_g) enters the conduction band and leaves behind a positively charged *hole* (h^+ , the absence of a bonding electron) in the valence band. Both the electron and the hole reside in *delocalized* orbitals, and both can move in an electric field, much as electrons move in a metal. (Holes migrate when an electron in a nearby orbital moves to fill in the hole, thereby creating a new hole in the nearby orbital.) Electrons and holes move in opposite directions in an electric field.

Silicon, a semiconductor of great importance in electronics, has a band gap of 1.94×10^{-22} kJ, or 1.21 *electron volts* (eV). This is the energy needed to create one electron and one hole or, put another way, the energy needed to break one Si—Si bond. This energy can be supplied either thermally or by using light with a photon energy greater than the band gap. To excite one *mole* of electrons from the valence band to the conduction band, an energy of

$$\frac{6.022 \times 10^{23} \text{ electrons}}{\text{mol}} \times \frac{1.94 \times 10^{-22} \text{ kJ}}{\text{electron}} = 117 \text{ kJ/mol}$$

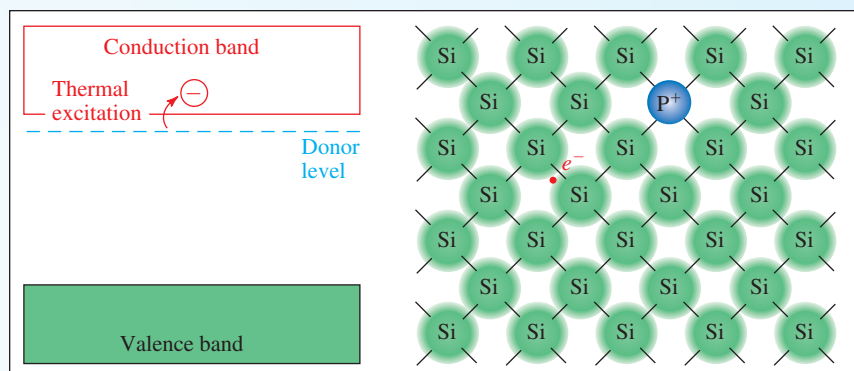
is required. For silicon, a large amount of energy is required, so there are very few mobile electrons and holes (about one electron in a trillion—i.e., 1 in 10^{12} —is excited thermally at room temperature); the conductivity of pure silicon is therefore about 10^{11} times lower than that of highly conductive metals such as silver. The number of electrons excited thermally is proportional to $e^{-E_g/2RT}$. Increasing the temperature or decreasing the band gap energy leads to higher conductivity for an intrinsic semiconductor. Insulators such as diamond and silicon dioxide (quartz), which have very large values of E_g , have conductivities 10^{15} to 10^{20} times lower than most metals.

The electrical conductivity of a semiconductor can be greatly increased by *doping* with impurities. For example, silicon, a Group 4A element, can be doped by adding small amounts of a Group 5A element, such as phosphorus, or a Group 3A element, such as boron. Figure (b) shows the effect of substituting phosphorus for silicon in the crystal structure (silicon has the same structure as diamond, Figure 13-31a). There are exactly enough valence band orbitals to accommodate four of the valence electrons from the phosphorus atom. However, a phosphorus atom has one more electron (and one more proton in its nucleus) than does silicon. The fifth electron enters a higher-energy orbital that is localized in the lattice near the phosphorus atom; the energy of this orbital, called a *donor level*, is just below the conduction band, within the energy gap. An electron in this orbital can easily become *delocalized* when a small amount of thermal energy promotes it into the conduction band. Because the phosphorus-doped silicon contains mobile, *negatively* charged carriers (electrons), it is said to be doped *n-type*. Doping the silicon crystal with boron produces a related, but opposite, effect. Each boron atom contributes only three valence electrons to bonding orbit-



A Generation of an electron–hole pair in silicon, an intrinsic semiconductor. The electron (e^-) and hole (h^+) have opposite charges, and so move in opposite directions in an electric field.

Semiconductor and effect of *n*-type doping on conduction properties.



Semiconductor and effect of *n*-type doping on conduction properties.

B *n*-type doping of silicon by phosphorus. The extra valence electron from a phosphorus atom is thermally excited into the conduction band, leaving a fixed positive charge on the phosphorus atom.

als in the valence band, and therefore a *hole* is localized near each boron atom. Thermal energy is enough to separate the negatively charged boron atom from the hole, delocalizing the latter. In this case the charge carriers are the holes, which are *positive*, and the crystal is doped *p*-type. In both *p*- and *n*-type doping, an extremely small concentration of dopants (as little as one part per billion) is enough to cause a significant increase in conductivity. For this reason, great pains are taken to purify the semiconductors used in electronic devices.

Even in a doped semiconductor, mobile electrons and holes are both present, although one carrier type is predominant. For example, in a sample of silicon doped with arsenic (*n*-type doping), the concentrations of mobile electrons are slightly less than the concentration of arsenic atoms (usually expressed in terms of atoms/cm³), and the concentrations of mobile holes are extremely low. Interestingly, the concentrations of electrons and holes always follow an equilibrium expression that is entirely analogous to that for the autodissociation of water into H⁺ and OH[−] ions (see Chapter 18); that is,

$$[e^-][h^+] = K_{\text{eq}}$$

where the equilibrium constant K_{eq} depends only on the identity of the semiconductor and the absolute temperature. For silicon at room temperature, $K_{\text{eq}} = 4.9 \times 10^{19}$ carriers²/cm⁶.

Doped semiconductors are extremely important in electronic applications. A *p*–*n* junction is formed by joining *p*- and *n*-type semiconductors. At the junction, free electrons and holes combine, annihilating each other and leaving positively and negatively charged dopant atoms on opposite sides. The unequal charge distribution on the two sides of the junction causes an electric field to develop and gives rise to current rectification (electrons can flow, with a small applied voltage, only from the *n* side to the *p* side of the junction; holes flow only in the reverse direction). Devices such as *diodes* and *transistors*, which form the bases of most analog and digital electronic circuits, are composed of *p*–*n* junctions.

PROFESSOR THOMAS A. MALLOUK
PENN STATE UNIVERSITY



R.E. Davis

The colors of semiconductors are determined by the band gap energy E_g . Only photons with energy greater than E_g can be absorbed. From the Planck radiation formula ($E = h\nu$) and $\lambda\nu = c$, we calculate that the wavelength, λ , of an absorbed photon must be less than hc/E_g . Gallium arsenide (GaAs; $E_g = 1.4$ eV) absorbs photons of wavelengths shorter than 890 nm, which is in the near infrared region. Because it absorbs all wavelengths of visible light, gallium arsenide appears black to the eye. Iron oxide (Fe₂O₃; $E_g = 2.2$ eV) absorbs light of wavelengths shorter than 570 nm; it absorbs both yellow and blue light, and therefore appears red. Cadmium sulfide (CdS; $E_g = 2.6$ eV), which absorbs blue light ($\lambda \leq 470$ nm), appears yellow. Strontium titanate (SrTiO₃; $E_g = 3.2$ eV) absorbs only in the ultraviolet ($\lambda \leq 390$ nm). It appears white to the eye because visible light of all colors is reflected by the fine particles.



A crystal can be cleaved into smaller crystals that have the same appearance as the larger crystal.

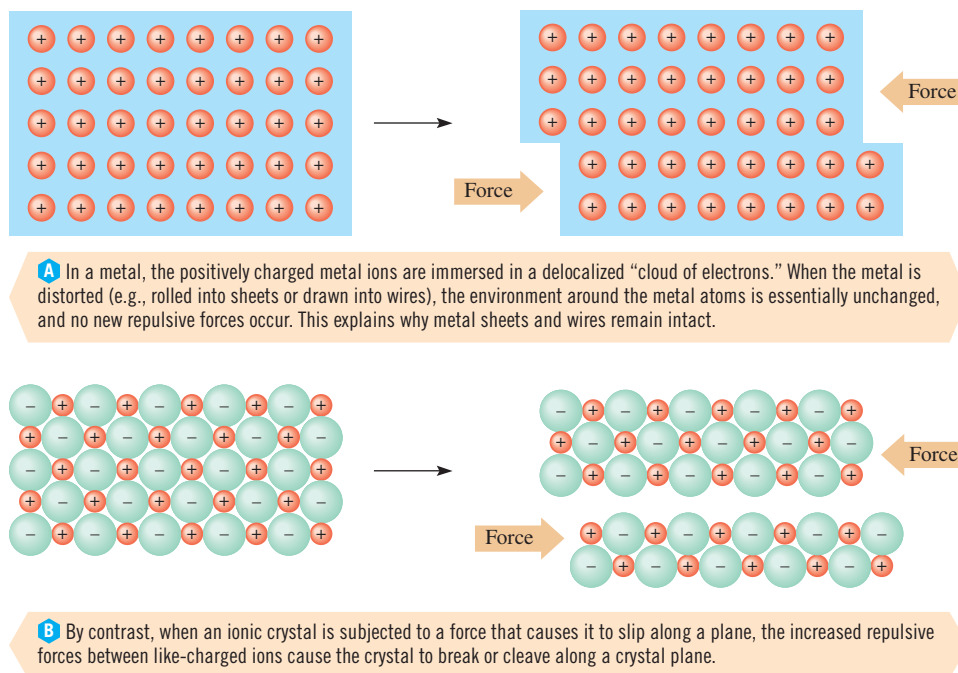


Figure 13-36

KEY TERMS

Adhesive force Force of attraction between a liquid and another surface.

Allotropes Different structural forms of the same element.

Amorphous solid A noncrystalline solid with no well-defined, ordered structure.

Band A series of very closely spaced, nearly continuous molecular orbitals that belong to the material as a whole.

Band gap (E_g) An energy separation between an insulator’s highest filled electron energy band and the next higher-energy vacant band.

Band theory of metals A theory that accounts for the bonding and properties of metallic solids.

Boiling point The temperature at which the vapor pressure of a liquid is equal to the external pressure; also the condensation point.

Capillary action The drawing of a liquid up the inside of a small-bore tube when adhesive forces exceed cohesive forces, or the depression of the surface of the liquid when cohesive forces exceed adhesive forces.

Clausius-Clapeyron equation An equation that relates the change in vapor pressure of a liquid to the change in its temperature and its molar heat of vaporization.

Cohesive forces All the forces of attraction among particles of a liquid.

Condensation The process by which a gas or vapor becomes a liquid; liquefaction.

Condensed phases The liquid and solid phases; phases in which particles interact strongly.

Conduction band A partially filled band or a band of vacant energy levels just higher in energy than a filled band; a band

within which, or into which, electrons must be promoted to allow electrical conduction to occur in a solid.

Coordination number In describing crystals, the number of nearest neighbors of an atom or ion.

Critical point The combination of critical temperature and critical pressure of a substance.

Critical pressure The pressure required to liquefy a gas (vapor) at its critical temperature.

Critical temperature The temperature above which a gas cannot be liquefied; the temperature above which a substance cannot exhibit distinct gas and liquid phases.

Crystal lattice The pattern of arrangement of particles in a crystal.

Crystalline solid A solid characterized by a regular, ordered arrangement of particles.

Deposition The direct solidification of a vapor by cooling; the reverse of sublimation.

Dipole-dipole interactions Interactions between polar molecules, that is, between molecules with permanent dipoles.

Dipole-induced dipole interaction See *Dispersion forces*.

Dispersion forces Very weak and very short-range attractive forces between short-lived temporary (induced) dipoles; also known as *London forces* or *van der Waals forces*.

Distillation The separation of a liquid mixture into its components on the basis of differences in boiling points.

Dynamic equilibrium A situation in which two (or more) processes occur at the same rate so that no net change occurs.

Enthalpy of fusion See *Heat of fusion*.

Enthalpy of solidification See *Heat of solidification*.

Evaporation The process by which molecules on the surface of a liquid break away and go into the gas phase.

Freezing point See *Melting point*.

Heat of condensation The amount of heat that must be removed from a specific amount of a vapor at its condensation point to condense the vapor with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the *molar heat of condensation*.

Heat of fusion The amount of heat required to melt a specific amount of a solid at its melting point with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the *molar heat of fusion*.

Heat of solidification The amount of heat that must be removed from a specific amount of a liquid at its freezing point to freeze it with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the *molar heat of solidification*.

Heat of vaporization The amount of heat required to vaporize a specific amount of a liquid at its boiling point with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the *molar heat of vaporization*.

Hydrogen bond A fairly strong dipole–dipole interaction (but still considerably weaker than covalent or ionic bonds) between molecules containing hydrogen directly bonded to a small, highly electronegative atom, such as N, O, or F.

Insulator A poor conductor of electricity and heat.

Intermolecular forces Forces *between* individual particles (atoms, molecules, ions) of a substance.

Intramolecular forces Forces between atoms (or ions) *within* molecules (or formula units).

Isomorphous Refers to crystals having the same atomic arrangement.

LeChatelier's Principle A system at equilibrium, or striving to attain equilibrium, responds in such a way as to counteract any stress placed upon it.

London forces See *Dispersion forces*.

Melting point The temperature at which liquid and solid coexist in equilibrium; also the freezing point.

Meniscus The upper surface of a liquid in a cylindrical container.

Metallic bonding Bonding within metals due to the electrical attraction of positively charged metal ions for mobile electrons that belong to the crystal as a whole.

Molar enthalpy of vaporization See *Molar heat of vaporization*.

Molar heat capacity The amount of heat necessary to raise the temperature of one mole of a substance one degree Celsius with no change in state; usually expressed in kJ/mol · °C. See *Specific heat*.

Molar heat of condensation The amount of heat that must be removed from one mole of a vapor at its condensation point to condense the vapor with no change in temperature; usually expressed in kJ/mol. See *Heat of condensation*.

Molar heat of fusion The amount of heat required to melt one mole of a solid at its melting point with no change in temperature; usually expressed in kJ/mol. See *Heat of fusion*.

Molar heat of vaporization The amount of heat required to vaporize one mole of a liquid at its boiling point with no change in temperature; usually expressed in kJ/mol. See *Heat of vaporization*.

Normal boiling point The temperature at which the vapor pressure of a liquid is equal to one atmosphere pressure.

Normal melting point The melting (freezing) point at one atmosphere pressure.

Phase diagram A diagram that shows equilibrium temperature–pressure relationships for different phases of a substance.

Polymorphous Refers to substances that crystallize in more than one crystalline arrangement.

Semiconductor A substance that does not conduct electricity well at low temperatures but that does at higher temperatures.

Specific heat The amount of heat necessary to raise the temperature of a specific amount of a substance one degree Celsius with no change in state; usually expressed in J/g · °C. See *Molar heat capacity*.

Sublimation The direct vaporization of a solid by heating without passing through the liquid state.

Supercritical fluid A substance at a temperature above its critical temperature. A supercritical fluid cannot be described as either a liquid or gas, but has the properties of both.

Surface tension The result of inward intermolecular forces of attraction among liquid particles that must be overcome to expand the surface area.

Triple point The point on a phase diagram that corresponds to the only pressure and temperature at which three phases (usually solid, liquid, and gas) of a substance can coexist at equilibrium.

Unit cell The smallest repeating unit showing all the structural characteristics of a crystal.

van der Waals forces See *Dispersion forces*.

Vaporization See *Evaporation*.

Vapor pressure The partial pressure of a vapor in equilibrium with its parent liquid or solid.

Viscosity The tendency of a liquid to resist flow; the inverse of its fluidity.

Volatility The ease with which a liquid vaporizes.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

General Concepts

- What causes dispersion forces? What factors determine the strengths of dispersion forces between molecules?
- What is hydrogen bonding? Under what conditions can hydrogen bonds be formed?
- Which of the following substances have permanent dipole–dipole forces? (a) GeH_4 ; (b) molecular MgCl_2 ; (c) PI_3 ; (d) F_2O .
- Which of the following substances have permanent dipole–dipole forces? (a) molecular AlBr_3 ; (b) PCl_5 ; (c) NO ; (d) SeF_4 .
- For which of the substances in Exercise 3 are dispersion forces the only important forces in determining boiling points?
- For which of the substances in Exercise 4 are dispersion forces the only important forces in determining boiling points?
- For each of the following pairs of compounds, predict which compound would exhibit stronger hydrogen bonding. Justify your prediction. It may help to write a Lewis formula for each. (a) water, H_2O , or hydrogen sulfide, H_2S ; (b) dichloromethane, CH_2Cl_2 or fluoroamine, NH_2F ; (c) acetone, $\text{C}_3\text{H}_6\text{O}$ (contains a $\text{C}=\text{O}$ double bond) or ethanol, $\text{C}_2\text{H}_6\text{O}$ (contains one $\text{C}-\text{O}$ single bond).
- Which of the following substances exhibits strong hydrogen bonding in the liquid and solid states? (a) CH_3OH (methanol); (b) PH_3 ; (c) CH_4 ; (d) $(\text{CH}_3)_2\text{NH}$; (e) CH_3NH_2 .
- Describe the intermolecular forces that are present in each of the following compounds. Which kind of force would have the greatest influence on the properties of each compound? (a) bromine pentafluoride, BrF_5 ; (b) acetone, $\text{C}_3\text{H}_6\text{O}$ (contains a central $\text{C}=\text{O}$ double bond); (c) formaldehyde, H_2CO .
- Describe the intermolecular forces that are present in each of the following compounds. Which kind of force would have the greatest influence on the properties of each compound? (a) ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ (contains one $\text{C}-\text{O}$ single bond); (b) phosphine, PH_3 ; (c) sulfur hexafluoride, SF_6 .
- Account for the fact that ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) is less viscous than glycerine ($\text{HOCH}_2\text{CHOHCH}_2\text{OH}$), but more viscous than ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$).
- Hydrogen bonding is a very strong dipole–dipole interaction. Why is hydrogen bonding so strong in comparison with other dipole–dipole interactions?
- Which of the following substances exhibits strong hydrogen bonding in the liquid and solid states? (a) H_2S ; (b) NH_3 ; (c) SiH_4 ; (d) HF ; (e) HCl .
- The molecular weights of SiH_4 and PH_3 are nearly the same. Account for the fact that the melting and boiling points of PH_3 (-133°C and -88°C) are higher than those of SiH_4 (-185°C and -112°C).
- Give an example of each of the six types of phase changes.
- For each of the following pairs of compounds, predict which would exhibit hydrogen bonding. Justify your prediction. It may help to write a Lewis formula for each. (a) ammonia, NH_3 , or phosphine, PH_3 ; (b) ethylene, C_2H_4 , or hydrazine, N_2H_4 ; (c) hydrogen fluoride, HF , or hydrogen chloride, HCl .
- ▲ Imagine replacing one H atom of a methane molecule, CH_4 , with another atom or group of atoms. Account for the order in the normal boiling points of the resulting compounds: CH_4 (-161°C); CH_3Br (3.59°C); CH_3F (-78°C); CH_3OH (65°C).
- Suppose you examine samples of copper (a pre-1982 penny is nearly pure copper), rubbing alcohol, and nitrogen (air is mostly nitrogen). Which one is a solid, which one is a liquid, and which one is a gas? How can you tell? What did you observe? How is the solid different from the liquid? How is the liquid different from the gas? Imagine a group of atoms or molecules of each of these substances. What do they look like? Are they in an organized or random arrangement? How far apart are they? How fast are they moving?
- Why does HF have a lower boiling point and lower heat of vaporization than H_2O , even though their molecular weights are nearly the same and the hydrogen bonds between molecules of HF are stronger?
- Consider the following substances: sodium fluoride (NaF), chlorine monofluoride (ClF), hydrogen fluoride (HF), and fluorine (F_2). (a) What type of particles does each substance have? (b) What type of intermolecular attractive forces hold the particles together in each substance? The table below lists the melting point (mp), boiling point (bp), density (D), and solubility in water of each of these substances.

	mp, $^\circ\text{C}$	bp, $^\circ\text{C}$	D , g/L	Solubility
NaF	993	1700	2558 (s)	4.13 g/100 g
ClF	-156	-100	2.43 (g)	violent reaction
HF	-84	20	0.922 (g)	miscible
F_2	-220	-188	1.69 (g)	mild reaction

- (c) Based on this information, determine the relative strengths of the forces holding the particles together.
 (d) List the intermolecular attractive forces in order of increasing strength.

The Liquid State

21. Use the kinetic-molecular theory to describe the behavior of liquids with changing temperature. Why are liquids denser than gases?
22. Within each group, assign each of the boiling points to the appropriate substance on the basis of intermolecular forces. (a) Ne, Ar, Kr: -246°C , -186°C , -152°C ; (b) NH_3 , H_2O , HF : -33°C , -20°C , 100°C .
23. Imagine a 250-mL beaker half full of acetone, CH_3COCH_3 , sitting in a laboratory in which the air pressure is 760 torr. The acetone is heated to 56°C , which causes its vapor pressure to increase to 760 torr. At this temperature, bubbles of the vapor form within the body of the liquid, rise to the surface, collapse, and release vaporized molecules. (a) What is this process called? (b) What effect, if any, would each of the following changes have on the temperature at which this process occurs:
 - (1) adding acetone to the beaker,
 - (2) removing some acetone from the beaker,
 - (3) increasing the atmospheric pressure,
 - (4) decreasing the atmospheric pressure,
 - (5) increasing the amount of heat being added to the acetone?
24. (a) What is the definition of the normal boiling point? (b) Why is it necessary to specify the atmospheric pressure over a liquid when measuring a boiling point?
25. Within each group, assign each of the boiling points to the respective substances on the basis of intermolecular forces. (a) N_2 , HCN , C_2H_6 : -196°C , -89°C , 26°C ; (b) H_2 , HCl , Cl_2 : -35°C , -259°C , -85°C .
26. What type of intermolecular forces must be overcome in converting each of the following from a liquid to a gas? (a) CO_2 ; (b) NH_3 ; (c) CHCl_3 ; (d) CCl_4 .
27. What factors determine how viscous a liquid is? How does viscosity change with increasing temperature?
28. What is the surface tension of a liquid? What causes this property? How does surface tension change with increasing temperature?
29. Dispersion forces are extremely weak in comparison to the other intermolecular attractions. Explain why this is so.
30. What are some of the similarities of the molecular-level descriptions of the viscosity, surface tension, vapor pressure, and rate of evaporation of a liquid?
31. What happens inside a capillary tube when a liquid “wets” the tube? What happens when a liquid does not “wet” the tube?
32. Choose from each pair the substance that, in the liquid state, would have the greater vapor pressure at a given temperature. Base your choice on predicted strengths of intermolecular forces. (a) BiBr_3 or BiCl_3 ; (b) CO or CO_2 ; (c) N_2 or NO ; (d) CH_3COOH or HCOOCH_3 .
33. Repeat Exercise 32 for (a) C_2H_6 or C_2Cl_6 ; (b) $\text{F}_2\text{C}=\text{O}$ or CH_3OH ; (c) He or H_2 .
34. The temperatures at which the vapor pressures of the following liquids are all 100 torr are given. Predict the order of increasing boiling points of the liquids: butane, C_4H_{10} , -44.2°C ; 1-butanol, $\text{C}_4\text{H}_{10}\text{O}$, 70.1°C ; diethyl ether, $\text{C}_4\text{H}_{10}\text{O}$, -11.5°C .
35. Plot a vapor pressure curve for GaCl_3 from the following vapor pressures. Determine the boiling point of GaCl_3 under a pressure of 250 torr from the plot:

$t(^{\circ}\text{C})$	91	108	118	132	153	176	200
vp (torr)	20.	40.	60.	100.	200.	400.	760.
36. Plot a vapor pressure curve for Cl_2O_7 from the following vapor pressures. Determine the boiling point of Cl_2O_7 under a pressure of 125 torr from the plot:

$t(^{\circ}\text{C})$	-24	-13	-2	10	29	45	62	79
vp (torr)	5.0	10.	20.	40.	100.	200.	400.	760.
37. The vapor pressure of liquid bromine at room temperature is 168 torr. Suppose that bromine is introduced drop by drop into a closed system containing air at 775 torr and room temperature. (The volume of liquid bromine is negligible compared to the gas volume.) If the bromine is added until no more vaporizes and a few drops of liquid are present in the flask, what would be the total pressure? What would be the total pressure if the volume of this closed system were decreased to one half its original value at the same temperature?
38. Which of the following compounds would be expected to form intermolecular hydrogen bonds in the liquid state? (a) CH_3OCH_3 (dimethyl ether); (b) CH_4 ; (c) HF ; (d) $\text{CH}_3\text{CO}_2\text{H}$ (acetic acid); (e) Br_2 ; (f) CH_3OH (methanol)
39. ΔH_{vap} is usually greater than ΔH_{fus} for a substance, yet the *nature* of interactions that must be overcome in the vaporization and fusion processes are similar. Why is ΔH_{vap} greater?
40. The heat of vaporization of water at 100°C is 2.26 kJ/g; at 37°C (body temperature), it is 2.41 kJ/g. (a) Convert the latter value to standard molar heat of vaporization, $\Delta H^{\circ}_{\text{vap}}$, at 37°C . (b) Why is the heat of vaporization greater at 37°C than at 100°C ?
41. Plot a vapor pressure curve for $\text{C}_2\text{Cl}_2\text{F}_4$ from the following vapor pressures. Determine the boiling point of $\text{C}_2\text{Cl}_2\text{F}_4$ under a pressure of 300. torr from the plot:

$t(^{\circ}\text{C})$	-95.4	-72.3	-53.7	-39.1	-12.0	3.5
vp (torr)	1.0	10.	40.	100.	400.	760.
42. Plot a vapor pressure curve for $\text{C}_2\text{H}_4\text{F}_2$ from the following vapor pressures. From the plot, determine the boiling point of $\text{C}_2\text{H}_4\text{F}_2$ under a pressure of 200. torr.

$t(^{\circ}\text{C})$	-77.2	-51.2	-31.1	-15.0	14.8	31.7
vp (torr)	1.0	10.	40.	100.	400.	760.



Phase Changes and Associated Heat Transfer

The following values for water will be useful in some exercises in this section. Values for some other substances appear in Appendix E.

Specific heat of ice	2.09 J/g · °C
Heat of fusion of ice at 0°C	334 J/g
Specific heat of liquid H ₂ O	4.184 J/g · °C
Heat of vaporization of liquid H ₂ O at 100°C	2.26×10^3 J/g
Specific heat of steam	2.03 J/g · °C

43. What amount of heat energy, in joules, must be removed to condense 25.4 g of water vapor at 122.5°C to liquid at 23.1°C?
44. What is the total quantity of heat energy transfer required to change 0.50 mol ice at -5°C to 0.50 mol steam at 100°C?
45. Which of the following changes of state are exothermic? Explain. (a) fusion; (b) liquefaction; (c) sublimation; (d) deposition.
46. Is the equilibrium that is established between two physical states of matter an example of static or dynamic equilibrium? How could one demonstrate the type of equilibrium established? Explain your answer.
47. The molar enthalpy of vaporization of methanol is 38.0 kJ/mol at 25°C. How much heat energy transfer is required to convert 250. mL of the alcohol from liquid to vapor? The density of CH₃OH is 0.787 g/mL at 25°C.
48. Suppose 50.0 g of solid bromine at its melting point of -7.2°C is heated, eventually producing gaseous bromine at 100.0°C. Which one of the following steps requires the most heat energy: melting the solid bromine, heating the liquid bromine from its melting point to its boiling point, boiling the bromine, or heating the gaseous bromine from its boiling point to 100.0°C?
 heat of fusion for bromine = 66.15 J/g
 specific heat of liquid bromine = 0.473 J/g · °C
 boiling point of bromine = 58.7°C
 heat of vaporization for bromine = 193.21 J/g
 specific heat of gaseous bromine 0.225 J/g · °C
49. Calculate the amount of heat required to convert 65.0 g of ice at 0°C to liquid water at 100.°C.
50. Calculate the amount of heat required to convert 80.0 g of ice at -15.0°C to steam at 125.0°C
51. Use data in Appendix E to calculate the amount of heat required to warm 165. g of mercury from 25°C to its boiling point and then to vaporize it.
52. If 250. g of liquid water at 100°C and 525 g of water at 30.0°C are mixed in an insulated container, what is the final temperature?
53. If 10.0 g of ice at -10.0°C and 20.0 g of liquid water at 100.°C are mixed in an insulated container, what will the final temperature be?
54. If 180. g of liquid water at 0°C and 18.0 g of steam at 110.°C are mixed in an insulated container, what will the final temperature be?
55. Water can be cooled in hot climates by the evaporation of water from the surfaces of canvas bags. What mass of water can be cooled from 35.0°C to 25.0°C by the evaporation of one gram of water? Assume that ΔH_{vap} does not change with temperature.

56. (a) How much heat must be removed to prepare 14.0 g of ice at 0.0°C from 14.0 g of water at 25.0°C? (b) Calculate the mass of water at 100.0°C that could be cooled to 23.5°C by the same amount of heat as that calculated in part (a).

Clausius–Clapeyron Equation

57. Toluene, C₆H₅CH₃, is a liquid used in the manufacture of TNT. Its normal boiling point is 111.0°C, and its molar heat of vaporization is 35.9 kJ/mol. What would be the vapor pressure (torr) of toluene at 85.00°C?
58. At their normal boiling points, the heat of vaporization of water (100°C) is 40,656 J/mol and that of heavy water (101.41°C) is 41,606 J/mol. Use these data to calculate the vapor pressure of each liquid at 80.00°C.
59. (a) Use the Clausius–Clapeyron equation to calculate the temperature (°C) at which pure water would boil at a pressure of 400.0 torr. (b) Compare this result with the temperature read from Figure 13-13. (c) Compare the results of (a) and (b) with a value obtained from Appendix E.
60. ▲ Show that the Clausius–Clapeyron equation can be written as

$$\ln P = \frac{-\Delta H_{\text{vap}}}{RT} + B$$

where B is a constant that has different values for different substances. This is an equation for a straight line. (a) What is the expression for the slope of this line? (b) Using the following vapor pressure data, plot $\ln P$ vs. $1/T$ for ethyl acetate, CH₃COOC₂H₅, a common organic solvent used in nail polish removers.

$t(^{\circ}\text{C})$	-43.4	-23.5	-13.5	-3.0	+9.1
vp (torr)	1	5	10.	20.	40.
$t(^{\circ}\text{C})$	+16.6	+27.0	+42.0	+59.3	
vp (torr)	60.	100.	200.	400.	

- (c) From the plot, estimate ΔH_{vap} for ethyl acetate.
- (d) From the plot, estimate the normal boiling point of ethyl acetate.



Products containing ethyl acetate

61. ▲ Repeat Exercise 60(b) and 60(c) for mercury, using the following data for liquid mercury. Then compare this value with the one in Appendix E.

$t(^{\circ}\text{C})$	126.2	184.0	228.8	261.7	323.0
vp (torr)	1	10.	40.	100.	400.

62. Isopropyl alcohol, $\text{C}_3\text{H}_8\text{O}$, is marketed as “rubbing alcohol.” Its vapor pressure is 100. torr at 39.5°C and 400. torr at 67.8°C . Estimate the molar heat of vaporization of isopropyl alcohol.
63. Using data from Exercise 62, predict the normal boiling point of isopropyl alcohol.
64. Boiling mercury is often used in diffusion pumps to attain a very high vacuum; pressures down to 10^{-10} atm can be readily attained with such a system. Mercury vapor is very toxic to inhale, however. The normal boiling point of liquid mercury is 357°C . What would be the vapor pressure of mercury at 25°C ?

Phase Diagrams

65. How many phases exist at a triple point? Describe what would happen if a small amount of heat were added under constant-volume conditions to a sample of water at the triple point. Assume a negligible volume change during fusion.
66. What is the critical point? Will a substance always be a liquid below the critical temperature? Why or why not?

Refer to the phase diagram of CO_2 in Figure 13-17b to answer Exercises 67–70.

67. What phase of CO_2 exists at 1.25 atm pressure and a temperature of (a) -90°C ; (b) -60°C ; (c) 0°C ?
68. What phases of CO_2 are present (a) at a temperature of -78°C and a pressure of 1.0 atm? (b) at -57°C and a pressure of 5.2 atm?
69. List the phases that would be observed if a sample of CO_2 at 10 atm pressure were heated from -80°C to -40°C .
70. How does the melting point of CO_2 change with pressure? What does this indicate about the relative density of solid CO_2 versus liquid CO_2 ?
71. ▲ You are given the following data for ethanol, $\text{C}_2\text{H}_5\text{OH}$.

Normal melting point	-117°C
Normal boiling point	78.0°C
Critical temperature	243°C
Critical pressure	63.0 atm

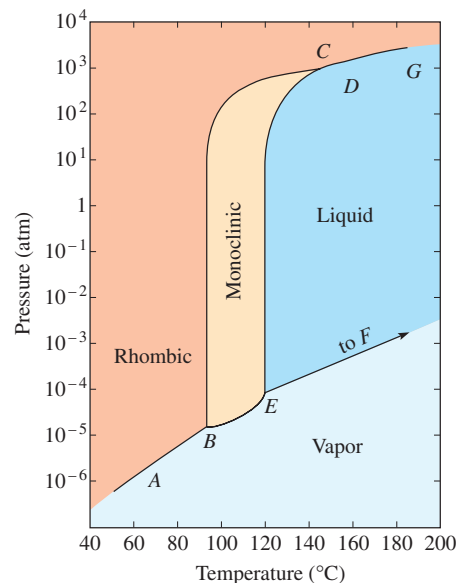
Assume that the triple point is slightly lower in temperature than the melting point and that the vapor pressure at the triple point is about 10^{-5} torr. (a) Sketch a phase diagram for ethanol. (b) Ethanol at 1 atm and $140.^\circ\text{C}$ is compressed to 70. atm. Are two phases present at any time during this process? (c) Ethanol at 1 atm and $270.^\circ\text{C}$ is compressed to 70. atm. Are two phases present at any time during this process?

72. ▲ You are given the following data for butane, C_4H_{10} .

Normal melting point	-138°C
Normal boiling point	0°C
Critical temperature	152°C
Critical pressure	38 atm

Assume that the triple point is slightly lower in temperature than the melting point and that the vapor pressure at the triple point is 3×10^{-5} torr. (a) Sketch a phase diagram for butane. (b) Butane at 1 atm and 140°C is compressed to 40 atm. Are two phases present at any time during this process? (c) Butane at 1 atm and 200°C is compressed to 40 atm. Are two phases present at any time during this process?

Exercises 73 and 74 refer to the phase diagram for sulfur. (The vertical axis is on a logarithmic scale.) Sulfur has two *solid* forms, monoclinic and rhombic.



Phase diagram for sulfur

73. ▲ (a) How many triple points are there for sulfur? (b) Indicate the approximate pressure and temperature at each triple point. (c) Which phases are in equilibrium at each triple point?
74. Which physical states should be present at equilibrium under the following conditions? (a) 10^{-1} atm and 110°C ; (b) 10^{-5} atm and 80°C ; (c) 5×10^3 atm and 160°C ; (d) 10^{-1} atm and 80°C ; (e) 10^{-5} atm and 140°C ; (f) 1 atm and 140°C .

The Solid State

75. ▲ Comment on the following statement: “The only perfectly ordered state of matter is the crystalline state.”
76. ● ▲ Ice floats in water. Why? Would you expect solid mercury to float in liquid mercury at its freezing point? Explain.
77. ● ▲ Distinguish among and compare the characteristics of molecular, covalent, ionic, and metallic solids. Give two examples of each kind of solid.
78. ● ▲ Classify each of the following substances, in the solid state, as molecular, ionic, covalent (network), or metallic solids:

	Melting Point ($^\circ\text{C}$)	Boiling Point ($^\circ\text{C}$)	Electrical Conductor	
			Solid	Liquid
MoF_6	17.5 (at 406 torr)	35	no	no
BN	3000 (sublimes)	—	no	no
Se_8	217	684	poor	poor
Pt	1769	3827	yes	yes
RbI	642	1300	no	yes



79. Classify each of the following substances, in the solid state, as molecular, ionic, covalent (network), or metallic solids:

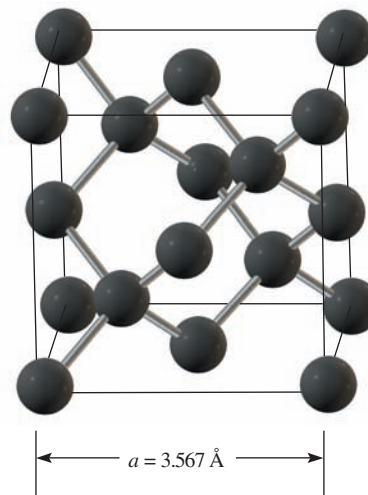
	Melting Point (°C)	Boiling Point (°C)	Electrical Conductor	
			Solid	Liquid
CeCl ₃	848	1727	no	yes
Ti	1675	—	yes	yes
TiCl ₄	−25	136	no	no
NO ₃ F	−175	−45.9	no	no
B	2300	2550	no	no

80. Based only on their formulas, classify each of the following in the solid state as a molecular, ionic, covalent (network), or metallic solid: (a) SO₂F; (b) MgF₂; (c) W; (d) Pb; (e) PF₅.
81. Based only on their formulas, classify each of the following in the solid state as a molecular, ionic, covalent (network), or metallic solid: (a) Au; (b) NO₂; (c) CaF₂; (d) SF₄; (e) C_{diamond}.
82. Arrange the following solids in order of increasing melting points and account for the order: NaF, MgF₂, AlF₃.
83. Arrange the following solids in order of increasing melting points and account for the order: MgO, CaO, SrO, BaO.

Unit Cell Data: Atomic and Ionic Sizes

84. Distinguish among and sketch simple cubic, body-centered cubic (bcc), and face-centered cubic (fcc) lattices. Use CsCl, sodium, and nickel as examples of solids existing in simple cubic, bcc, and fcc lattices, respectively.
85. Describe a unit cell as precisely as you can.
86. Determine the number of ions of each type present in each unit cell shown in Figure 13-29.
87. Refer to Figure 13-29a. (a) If the unit cell edge is represented as a , what is the distance (center to center) from Cs⁺ to its nearest neighbor? (b) How many equidistant nearest neighbors does each Cs⁺ ion have? What are the identities of these nearest neighbors? (c) What is the distance (center to center), in terms of a , from a Cs⁺ ion to the nearest Cs⁺ ion? (d) How many equidistant nearest neighbors does each Cl[−] ion have? What are their identities?
88. Refer to Figure 13-28. (a) If the unit cell edge is represented as a , what is the distance (center to center) from Na⁺ to its nearest neighbor? (b) How many equidistant nearest neighbors does each Na⁺ ion have? What are the identities of these nearest neighbors? (c) What is the distance (center to center), in terms of a , from a Na⁺ ion to the nearest Na⁺ ion? (d) How many equidistant nearest neighbors does each Cl[−] ion have? What are their identities?
89. Polonium crystallizes in a simple cubic unit cell with an edge length of 3.36 Å. (a) What is the mass of the unit cell? (b) What is the volume of the unit cell? (c) What is the theoretical density of Po?

90. Calculate the density of Na metal. The length of the body-centered cubic unit cell is 4.24 Å.
91. Gold crystallizes into a face-centered structure, and its density is 19.3 g/cm³. What is the length of an edge of the unit cell in nm?
92. The atomic radius of iridium is 1.36 Å. The unit cell of iridium is a face-centered cube. Calculate the density of iridium.
93. A certain metal has a specific gravity of 10.200 at 25°C. It crystallizes in a body-centered cubic arrangement with a unit cell edge length of 3.147 Å. Determine the atomic weight, and identify the metal.
94. The structure of diamond follows, with each sphere representing a carbon atom. (a) How many carbon atoms are there per unit cell in the diamond structure? (b) Verify, by extending the drawing if necessary, that each carbon atom has four nearest neighbors. What is the arrangement of these nearest neighbors? (c) What is the distance (center to center) from any carbon atom to its nearest neighbor, expressed in terms of a , the unit cell edge? (d) The observed unit cell edge length in diamond is 3.567 Å. What is the C—C single bond length in diamond? (e) Calculate the density of diamond.



Structure of diamond

95. The crystal structure of CO₂ is cubic, with a cell edge length of 5.540 Å. A diagram of the cell is shown in Figure 13-31a. (a) What is the number of molecules of CO₂ per unit cell? (b) Is this structure face-centered cubic? How can you tell? (c) What is the density of solid CO₂ at this temperature?
96. A Group 4A element with a density of 11.35 g/cm³ crystallizes in a face-centered cubic lattice whose unit cell edge length is 4.95 Å. Calculate its atomic weight. What is the element?
97. Crystalline silicon has the same structure as diamond, with a unit cell edge length of 5.430 Å. (a) What is the Si—Si distance in this crystal? (b) Calculate the density of crystalline silicon.
98. (a) What types of electromagnetic radiation are suitable for diffraction studies of crystals? (b) Describe the X-ray diffraction experiment. (c) What must be the relationship between the wavelength of incident radiation and the spacing of the particles in a crystal for diffraction to occur?

99. ▲ (a) Write the Bragg equation. Identify each symbol. (b) X-rays from a palladium source ($\lambda = 0.576 \text{ \AA}$) were reflected by a sample of copper at an angle of 9.408° . This reflection corresponds to the unit cell length ($d = a$) with $n = 2$ in the Bragg equation. Calculate the length of the copper unit cell.
100. The spacing between successive planes of platinum atoms parallel to the cubic unit cell face is $2.256 \text{ \AA}$. When X-radiation emitted by copper strikes a crystal of platinum metal, the minimum diffraction angle of X-rays is 19.98° . What is the wavelength of the Cu radiation?
101. Gold crystallizes in a fcc structure. When X-radiation of $0.70926 \text{ \AA}$ wavelength from molybdenum is used to determine the structure of metallic gold, the minimum diffraction angle of X-rays by the gold is 8.6838° . Calculate the spacing between parallel layers of gold atoms.

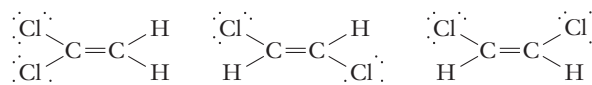
Metallic Bonding and Semiconductors

102. ● In general, metallic solids are ductile and malleable, whereas ionic salts are brittle and shatter readily (although they are hard). Explain this observation.
103. ● What single factor accounts for the ability of metals to conduct both heat and electricity in the solid state? Why are ionic solids poor conductors of heat and electricity although they are composed of charged particles?
104. Compare the temperature dependence of electrical conductivity of a metal with that of a typical metalloid. Explain the difference.

Mixed Exercises

105. Benzene, C_6H_6 , boils at 80.1°C . How much energy, in joules, would be required to change 450.0 g of liquid benzene at 21.5°C to a vapor at its boiling point? (The specific heat of liquid benzene is $1.74 \text{ J/g} \cdot ^\circ\text{C}$ and its heat of vaporization is 395 J/g .)
106. The three major components of air are N_2 (bp = -196°C), O_2 (bp = -183°C), and Ar (bp = -186°C). Suppose we have a sample of liquid air at -200°C . In what order will these gases evaporate as the temperature is raised?
107. ▲ A 20.0-g sample of liquid ethanol, $\text{C}_2\text{H}_5\text{OH}$, absorbs $6.84 \times 10^3 \text{ J}$ of heat at its normal boiling point, 78.0°C . The molar enthalpy of vaporization of ethanol, ΔH_{vap} , is 39.3 kJ/mol . (a) What volume of $\text{C}_2\text{H}_5\text{OH}$ vapor is produced? The volume is measured at 78.0°C and 1.00 atm pressure. (b) What mass of $\text{C}_2\text{H}_5\text{OH}$ remains in the liquid state?
108. Liquid ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, is one of the main ingredients in commercial antifreeze. Do you predict its viscosity to be greater or less than that of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$?
109. ▲ The boiling points of HCl, HBr, and HI increase with increasing molecular weight. Yet the melting and boiling points of the sodium halides, NaCl, NaBr, and NaI, decrease with increasing formula weight. Explain why the trends are opposite. Describe the intermolecular forces present in each of these compounds and predict which has the lowest boiling point.

110. The structures for three molecules having the formula $\text{C}_2\text{H}_2\text{Cl}_2$ are



Describe the intermolecular forces present in each of these compounds and predict which has the lowest boiling point.

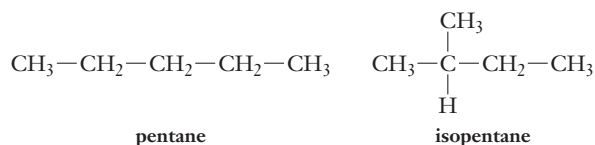
111. Are the following statements true or false? Indicate why if a statement is false. (a) The vapor pressure of a liquid will decrease if the volume of liquid decreases. (b) The normal boiling point of a liquid is the temperature at which the external pressure equals the vapor pressure of the liquid. (c) The vapor pressures of liquids in a similar series tend to increase with increasing molecular weight.
112. Are the following statements true or false? Indicate why if a statement is false. (a) The equilibrium vapor pressure of a liquid is independent of the volume occupied by the vapor above the liquid. (b) The normal boiling point of a liquid changes with changing atmospheric pressure. (c) The vapor pressure of a liquid will increase if the mass of liquid is increased.
113. The following are vapor pressures at 20°C . Predict the order of increasing normal boiling points of the liquids, acetone, 185 torr ; ethanol, 44 torr ; carbon disulfide, CS_2 , 309 torr .
114. Refer to Exercise 113. What is the expected order of increasing molar heats of vaporization, ΔH_{vap} , of these liquids at their boiling points? Account for the order.
115. Refer to the sulfur phase diagram in Exercises 73 and 74. (a) Can rhombic sulfur be sublimed? If so, under what conditions? (b) Can monoclinic sulfur be sublimed? If so, under what conditions? (c) Describe what happens if rhombic sulfur is slowly heated from 80°C to 140°C at constant 1-atm pressure. (d) What happens if rhombic sulfur is heated from 80°C to 140°C under constant pressure of $5 \times 10^{-6} \text{ atm}$?
116. The normal boiling point of ammonia, NH_3 , is -33°C , and its freezing point is -78°C . Fill in the blanks. (a) At STP (0°C , 1 atm pressure), NH_3 is a _____. (b) If the temperature drops to -40°C , the ammonia will _____ and become a _____. (c) If the temperature drops further to -80°C and the molecules arrange themselves in an orderly pattern, the ammonia will _____ and become a _____. (d) If crystals of ammonia are left on the planet Mars at a temperature of -100°C , they will gradually disappear by the process of _____ and form a _____.
117. Give the correct names for these changes in state: (a) Crystals of *para*-dichlorobenzene, used as a moth repellent, gradually become vapor without passing through the liquid phase. (b) As you enter a warm room from the outdoors on a cold winter day, your eyeglasses become fogged with a film of moisture. (c) On the same (windy) winter day, a pan of water is left outdoors. Some of it turns to vapor, the rest to ice.
118. The normal boiling point of trichlorofluoromethane, CCl_3F , is 24°C , and its freezing point is -111°C . Complete these sentences by supplying the proper terms that describe a state of matter or a change in state. (a) At standard



temperature and pressure, CCl_3F is a _____. (b) In an arctic winter at -40°C and 1 atm pressure, CCl_3F is a _____. If it is cooled to -120°C , the molecules arrange themselves in an orderly lattice, the CCl_3F _____ and becomes a _____. (c) If crystalline CCl_3F is held at a temperature of -120°C while a stream of helium gas is blown over it, the crystals will gradually disappear by the process of _____. If liquid CCl_3F is boiled at atmospheric pressure, it is converted to a _____ at a temperature of _____.

Conceptual Exercises

119. The van der Waals constants (see Section 12–15) are $a = 19.01 \text{ L}^2 \cdot \text{atm/mol}^2$, $b = 0.1460 \text{ L/mol}$ for pentane, and $a = 18.05 \text{ L}^2 \cdot \text{atm/mol}^2$, $b = 0.1417 \text{ L/mol}$ for isopentane.

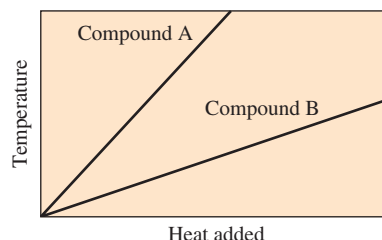


- (a) Basing your reasoning on intermolecular forces, why would you expect a for pentane to be greater? (b) Basing your reasoning on molecular size, why would you expect b for pentane to be greater?
120. What is contained in the bubbles formed during the boiling process?
121. How can one convert a sample of a liquid to a vapor without changing its temperature?
122. Iodine sublimates at room temperature and pressure; water does not. Explain the differences you would expect to observe at room temperature if 7.5 grams of iodine crystals were sealed in a 10.-mL container and 7.5 mL of water were sealed in a similar container.



Iodine sublimates

123. Using ball-and-stick representations, draw a sketch similar to Figure 13–3 of four molecules of HBr that indicates dipole–dipole forces between molecules.
124. Using space-filling representations, draw a sketch similar to Figure 13–3 of four molecules of HBr that indicates dipole–dipole forces between molecules.
125. Referring to the phase diagram for carbon dioxide shown in Figure 13–17b for approximate values, draw a heating curve similar to that in Figure 13–15 for carbon dioxide at 1 atmosphere pressure. Draw a second heating curve for carbon dioxide at 5 atm pressure. Estimate the transition temperatures.
126. A popular misconception is that “hot water freezes more quickly than cold water.” In an experiment, two 100.-mL samples of water, in identical containers, were placed far apart in a freezer at -25°C . One sample had an initial temperature of 78°C , while the other was at 24°C . The second sample took 151 minutes to freeze, and the warmer sample took 166 minutes. The warmer sample took more time but not much. How can you explain their taking about the same length of time to freeze?
127. Consider the portions of the heating curves shown here. Which compound has the highest specific heat capacity?



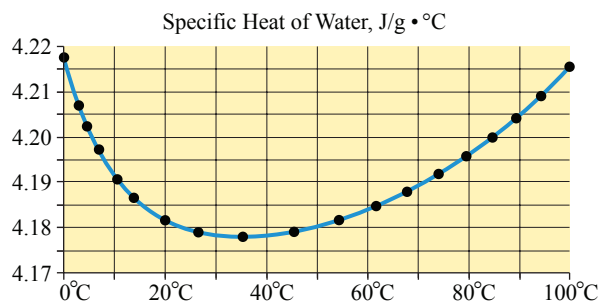
128. An unopened ice-cold can of Coca-Cola® is placed on the kitchen table in the summertime. After a while, drops of water are observed on the outside of the can. Where did they come from?
129. The element potassium (a metal) has a melting point of 63.65°C and a boiling point of 774°C . Suppose a sample of potassium at 100°C is cooled to room temperature (25°C). In what state of matter is the potassium at 100°C ? In what state of matter is the potassium at 25°C ? What term is used to describe the phase change, if any, that occurs as potassium is cooled from 100°C to 25°C ?

Building Your Knowledge

130. More than 150 years ago Pierre Dulong and A. T. Petit discovered a *rule of thumb* that the heat capacity of one mole of a pure solid element is about 6.0 calories per $^\circ\text{C}$ (i.e., about $25 \text{ J/}^\circ\text{C}$). A 100.2-g sample of an unknown metal at 99.9°C is placed in 50.6 g of water at 24.8°C . The temperature is 36.6°C when the system comes to equilibrium. Assume all heat lost by the metal is absorbed by the water. What is the likely identity of this metal?
131. In a flask containing dry air and some liquid silicon tetrachloride, SiCl_4 , the total pressure was 988 torr at 225°C . Halving the volume of the flask increased the pressure to 1742 torr at constant temperature. What is the vapor pressure of SiCl_4 in this flask at 225°C ?
132. A friend comes to you with this problem: “I looked up the vapor pressure of water in a table; it is 26.7 torr at 300

K and 92,826 torr at 600 K. That means that the vapor pressure increases by a factor of 3477 when the absolute temperature doubles over this temperature range. But I thought the pressure was proportional to the absolute temperature, $P = nRT/V$. The pressure doesn't just double. Why?" How would you help the friend?

133. Using as many as six drawings (frames) for each, depict the changes that occur at the molecular level during each of the following physical changes: (a) melting an ice cube; (b) sublimation of an ice cube below 4.6°C and 4.6 torr; and (c) evaporation of a droplet of water at room temperature and pressure.
134. Write the Lewis formula of each member of each of the following pairs. Then use VSEPR theory to predict the geometry about each central atom, and describe any features that lead you to decide which member of each pair would have the lower boiling point. (a) CH_3COOH and HCOCH_3 ; (b) NH_2F and BH_2Cl ; (c) $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OCH_3
135. At its normal melting point of 271.3°C, solid bismuth has a density of 9.73 g/cm³, and liquid bismuth has a density of 10.05 g/cm³. A mixture of liquid and solid bismuth is in equilibrium at 271.3°C. If the pressure were increased from 1 atm to 10 atm, would more solid bismuth melt or would more liquid bismuth freeze? What unusual property does bismuth share with water?
136. Although the specific heat of liquid water is usually given as 4.18 J/g°C, it actually varies with temperature, as shown in the graph below. At what temperatures are the deviations from the accepted value the greatest? What is the approximate percent error at these temperatures that have the greatest deviation?



Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

137. Using *The Merck Index* or *Handbook of Chemistry and Physics* or a suitable site found on the web, look up the temperature at which caffeine sublimates at standard atmospheric pressure.
138. (a) On the web locate the temperature and the pressure at the triple point of carbon dioxide and compare the data that you find with that in Figure 13-17 in the textbook. It is suggested that you follow these steps: Go to **webbook.nist.gov**, and click on "NIST Chemistry WebBook" and then "Formula." Enter CO_2 , and click on "Phase Change." If this route does not work, you will need to rely upon one of the search programs to help you find these data. (b) Repeat part (a) for water instead of carbon dioxide.
139. Go to www.ibiblio.org/e-notes/Cryst/Cryst.htm using a compatible browser. Click on Face Centered Cubic (FCC) and view the interactive unit cell model. (a) Sketch the atom arrangement in the top layer, middle layer, and bottom layer. What do you observe about the arrangement of the atoms in each layer? Which are the same? (b) Rotate the model to view another face and redraw the atom arrangement on the three layers. Do you observe any difference?
140. Open www.lyo-san.ca/english/lyophilisation.html. Using information at this site, at another site, or from reference books, compare the terms: lyophilization, freeze-drying, and sublimation.





Spreading a soluble salt such as calcium chloride, CaCl_2 , on icy roadways or sidewalks forms a solution with a lower freezing point than pure water. This causes the ice or snow to melt at a lower temperature and prevents the resulting salt solution from freezing until it reaches the same lower temperature. This lower temperature of melting or freezing is determined by the salt ion concentration (see Section 14-12).

iStockphoto.com/ollo

OUTLINE

The Dissolution Process

- 14-1 Spontaneity of the Dissolution Process
- 14-2 Dissolution of Solids in Liquids
- 14-3 Dissolution of Liquids in Liquids (Miscibility)
- 14-4 Dissolution of Gases in Liquids
- 14-5 Rates of Dissolution and Saturation
- 14-6 Effect of Temperature on Solubility
- 14-7 Effect of Pressure on Solubility
- 14-8 Molality and Mole Fraction

Colligative Properties of Solutions

- 14-9 Lowering of Vapor Pressure and Raoult's Law
- 14-10 Fractional Distillation
- 14-11 Boiling Point Elevation
- 14-12 Freezing Point Depression
- 14-13 Determination of Molecular Weight by Freezing Point Depression or Boiling Point Elevation
- 14-14 Colligative Properties and Dissociation of Electrolytes
- 14-15 Osmotic Pressure

Colloids

- 14-16 The Tyndall Effect
- 14-17 The Adsorption Phenomenon
- 14-18 Hydrophilic and Hydrophobic Colloids

OBJECTIVES

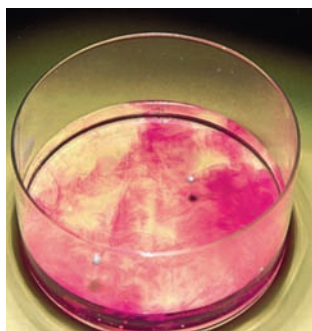
After you have studied this chapter, you should be able to

- ▶ Describe the factors that favor the dissolution process
- ▶ Describe the dissolution of solids in liquids, liquids in liquids, and gases in liquids
- ▶ Describe how temperature and pressure affect solubility
- ▶ Express concentrations of solutions in terms of molality and mole fractions
- ▶ Describe the four colligative properties of solutions and some of their applications
- ▶ Carry out calculations involving the four colligative properties of solutions: lowering of vapor pressure (Raoult's Law), boiling point elevation, freezing point depression, and osmotic pressure
- ▶ Use colligative properties to determine molecular weights of compounds
- ▶ Describe how dissociation and ionization of compounds affect colligative properties
- ▶ Recognize and describe colloids: the Tyndall effect, the adsorption phenomenon, and hydrophilic and hydrophobic colloids

A solution is defined as a *homogeneous mixture*, at the molecular level, of two or more substances in which phase separation does not occur. A solution consists of a solvent and one or more solutes, whose proportions can vary from one solution to another. By contrast, a pure substance has a fixed composition. The *solvent* is the medium in which the *solutes* are dissolved. Solute usually dissolve to give ions or molecules in solution.

Solutions include different combinations in which a solid, liquid, or gas acts as either solvent or solute. Usually the solvent is a liquid. For instance, seawater is an aqueous solution of many salts and some gases such as carbon dioxide and oxygen. Carbonated water is a saturated solution of carbon dioxide in water. Solutions are common in nature and are extremely important in all life processes, in all scientific inquiry, and in many industrial processes. Many naturally occurring fluids contain particulate matter suspended in a solution. For example, blood contains a solution (plasma) with suspended blood cells. Seawater contains dissolved substances as well as suspended solids. The body fluids of all life forms are solutions. Variations in concentrations of our bodily fluids, especially those of blood and urine, give physicians valuable clues about a person's health. Solutions in which the solvent is not a liquid are also common. Air is a solution of gases with variable composition. Dental fillings are solid amalgams, or solutions of liquid mercury dissolved in solid metals. Alloys are solid solutions of solids dissolved in a metal.

It is usually obvious which of the components of a solution is the solvent and which is (are) the solute(s): The solvent is usually the most abundant species present. In a cup of instant coffee, the coffee and any added sugar are considered solutes, and the hot water is the solvent. When both components are liquids, the decision is less clear. Though it is preferable to refer simply to the different components, the solute/solvent terminology is often used. If we mix 10 grams of alcohol with 90 grams of water, we would call alcohol the solute. If we mix 10 grams of water with 90 grams of alcohol, water would be considered the solute. But which is the solute and which is the solvent in a solution of 50 grams of water and 50 grams of alcohol? In such cases, the terminology is arbitrary with no set rules.



Charles Steele

Sodium reacts with water to form hydrogen gas and a solution of sodium hydroxide. A small amount of phenolphthalein indicator added to this solution turns pink due to the presence of sodium hydroxide.

The Dissolution Process

14-1 Spontaneity of the Dissolution Process

In Section 6-1, Part 5, we listed the solubility guidelines for aqueous solutions. Now we investigate the major factors that influence solubility.

A substance may dissolve with or without reaction with the solvent. For example, when metallic sodium reacts with water, bubbles of hydrogen are produced and a great deal of

Unless otherwise noted, all content on this page is © Cengage Learning.

heat is given off. A chemical change occurs in which H_2 and soluble ionic sodium hydroxide, NaOH , are produced.



If the resulting solution is evaporated to dryness, solid sodium hydroxide, NaOH , is obtained rather than metallic sodium. This, along with the production of hydrogen bubbles, is evidence of a reaction with the solvent. Reactions that involve oxidation state changes are usually considered to be chemical reactions and not dissolutions.

Solid sodium chloride, NaCl , on the other hand, dissolves in water with no evidence of chemical reaction.



Evaporation of the water from the sodium chloride solution yields the original NaCl . In this chapter we will focus on dissolution processes of this type, in which no irreversible reaction occurs between components.

The ease of dissolution of a solute depends on two factors that accompany the process: (1) the change in energy and (2) the change in disorder (called entropy change). In the next chapter we will study in detail how both of these factors influence many kinds of physical and chemical changes. For now, we point out that a process is *avored* by (1) a *decrease in the energy* of the system, which corresponds to an *exothermic process*, and (2) an *increase in the disorder*, or randomness, of the system.

Let us look at the first of these factors. The energy change that accompanies a dissolution process is called the **heat of solution**, $\Delta H_{\text{solution}}$. This change depends mainly on how strongly the solute and solvent particles interact. If a solution gets hotter as a substance dissolves, energy is being released in the form of heat. A negative value of $\Delta H_{\text{solution}}$ designates the release of heat, and the process is called *exothermic*. More negative (less positive) values of $\Delta H_{\text{solution}}$ favor the dissolution process.

In a pure liquid, all the intermolecular forces are between like molecules. When the liquid and a solute are mixed, each molecule then interacts with unlike molecules (or ions) as well as with like molecules. The relative strengths of these interactions help to determine the extent of solubility of a solute in a solvent. The main interactions that affect the dissolution of a solute in a solvent follow.

- Weak solute–solute attractions favor solubility.
- Weak solvent–solvent attractions favor solubility.
- Strong solvent–solute attractions favor solubility.

Figure 14-1 illustrates the interplay of these factors. The intermolecular or interionic attractions among solute particles in the pure solute must be overcome (Step a) to dissolve the solute. This part of the process requires an *absorption* of energy (*endothermic*). Separat-

► Ionic solutes that do not react with the solvent undergo solvation. This is a kind of process in which molecules of solvent are attracted, usually in oriented clusters, to the solute particles.



The ocean is a solution of many different dissolved compounds. In this chapter we look at solution formation and solution properties.

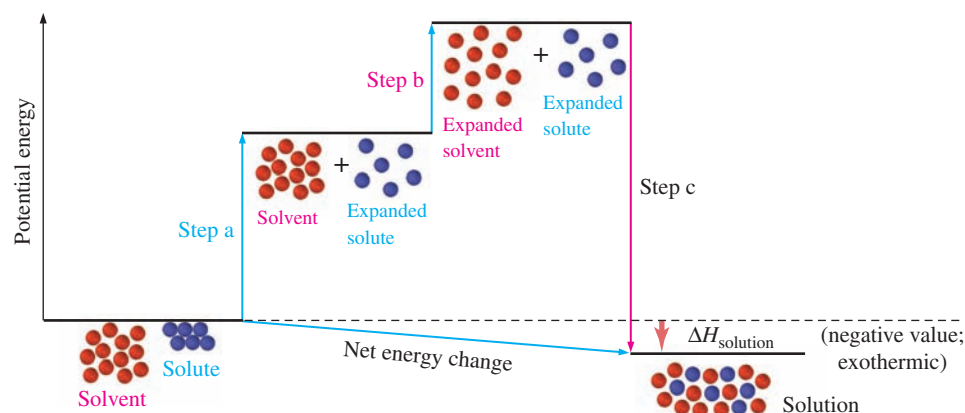
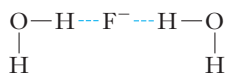


Figure 14-1 A diagram representing the changes in energy content associated with the hypothetical three-step sequence in a dissolution process—in this case, for a solid solute dissolving in a liquid solvent. (Similar considerations would apply to other combinations.) The process depicted here is exothermic. The amount of heat absorbed in Steps a and b is less than the amount released in Step c. In an *endothermic* process (not shown), the heat content of the solution would be *higher* than that of the original solvent plus solute. Thus, the amount of energy absorbed in Steps a and b would be *greater* than the amount of heat released in Step c.

Unless otherwise noted, all content on this page is © Cengage Learning.

► We can consider these energy changes separately, even though the actual process cannot be carried out in these separate steps.

► The dissolution of NaF in water is one of the few cases in which the dissolving process is not accompanied by an overall increase in disorder. The water molecules become more ordered around the small F^- ions. This is due to the strong hydrogen bonding between H_2O molecules and F^- ions.



The amount of heat released on mixing, however, outweighs the disadvantage of this ordering.

ing the solvent molecules from one another (Step b) to “make room” for the solute particles also requires the *absorption* of energy (endothermic). Energy is *released*, however, as the solute particles and solvent molecules interact in the solution (Step c, exothermic). The overall dissolution process is exothermic (and favored) if the amount of heat absorbed in hypothetical Steps a and b is less than the amount of energy released in Step c. The process is endothermic (and disfavored) if the amount of energy absorbed in Steps a and b is greater than the amount of heat released in Step c.

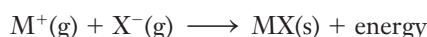
Many solids do dissolve in liquids by *endothermic* processes, however. The reason such processes can occur is that the endothermicity can be outweighed by a large increase in disorder of the solute during the dissolution process. The solute particles are highly ordered in a solid crystal, but are free to move about randomly in liquid solutions. Likewise, the degree of disorder in the solvent increases as the solution is formed, because solvent molecules are then in a more random environment. They are surrounded by a mixture of solvent and solute particles.

Most dissolving processes are accompanied by an overall increase in disorder. Thus, the disorder factor is usually *favorable* to solubility. The determining factor, then, is whether the heat of solution (energy) also favors dissolution or, if it does not, whether it is small enough to be outweighed by the favorable effects of the increasing disorder. In gases, for instance, the molecules are so far apart that intermolecular forces are quite weak. Thus, when gases are mixed, changes in the intermolecular forces are very slight. So the very favorable increase in disorder that accompanies mixing is always more important than possible changes in intermolecular attractions (energy). Hence, gases that do not react with one another can always be mixed in any proportion.

The most common types of solutions are those in which the solvent is a liquid. In the next several sections we consider liquid solutions in more detail.

14-2 Dissolution of Solids in Liquids

The ability of a solid to go into solution depends most strongly on its crystal lattice energy, or the strength of attractions among the particles making up the solid. The **crystal lattice energy** is defined as the energy change accompanying the formation of one mole of formula units in the crystalline state from constituent particles in the gaseous state. This process is always exothermic; that is, crystal lattice energies are always *negative*. For an ionic solid, the process is written as



The amount of energy involved in this process depends on the electrostatic attraction between ions in the solid. When these attractions are strong due to higher charges and/or small ion sizes, a large amount of energy is released as the solid forms, increasing its stability.

The reverse of the crystal formation reaction is breaking the crystal into separated gas phase ions.



This process can be considered the hypothetical first step (Step a in Figure 14-1) in forming a solution of a solid in a liquid. It is always endothermic. The smaller the magnitude of the crystal lattice energy (a measure of the solute–solute interactions), the more readily dissolution occurs because less energy must be supplied to start the dissolution process.

If the solvent is water, the energy that must be supplied to expand the solvent (Step b in Figure 14-1) includes that required to break up some of the hydrogen bonding between water molecules.

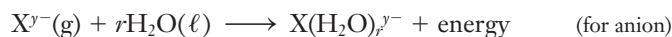
The third major factor contributing to the heat of solution is the extent to which solvent molecules interact with particles of the solid. The process in which solvent molecules surround and interact with solute ions or molecules is called **solvation**. When the solvent is water, the more specific term **hydration** is used. **Hydration energy** (equal to the sum of Steps b and c in Figure 14-1) is defined as the energy change involved in the (exothermic) hydration of one mole of gaseous ions.

STOP & THINK

A very negative crystal lattice energy indicates very strong attractions within the solid.

► Hydration energy is also referred to as the **heat of hydration**.

Unless otherwise noted, all content on this page is © Cengage Learning.



Hydration is usually highly exothermic for ionic or polar covalent compounds because the polar water molecules interact very strongly with ions and polar molecules. In fact, the only solutes that are appreciably soluble in water either undergo dissociation or ionization or are able to form hydrogen bonds with water.

The overall heat of solution for a solid dissolving in a liquid is equal to the heat of solvation minus the crystal lattice energy.

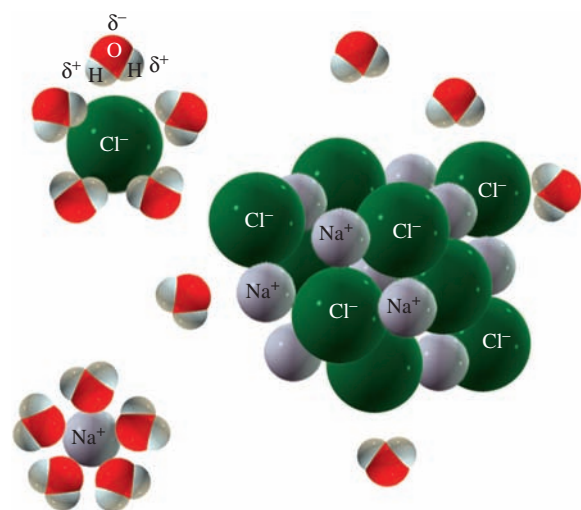
$$\Delta H_{\text{solution}} = (\text{heat of solvation}) - (\text{crystal lattice energy})$$

Remember that both terms on the right are always negative.

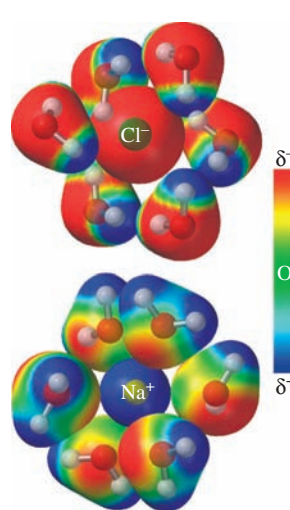
Nonpolar solids such as naphthalene, $C_{10}H_8$, do not dissolve appreciably in polar solvents such as water because the two substances do not attract each other significantly. This is true despite the fact that crystal lattice energies of solids consisting of nonpolar molecules are much less negative (smaller in magnitude) than those of ionic solids. Naphthalene dissolves readily in nonpolar solvents such as benzene because there are no strong attractive forces between solute molecules or between solvent molecules. In such cases, the increase in disorder controls the process. These facts help explain the observation that “like dissolves like.”

The statement “like dissolves like” means that polar solvents dissolve ionic and polar molecular solutes, and nonpolar solvents dissolve nonpolar molecular solutes.

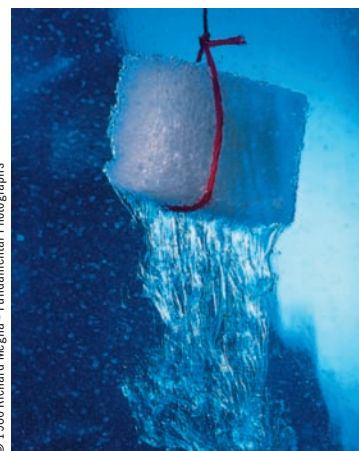
Consider what happens when a piece of sodium chloride, a typical ionic solid, is placed in water. The δ^+ parts of water molecules (H atoms) attract the negative chloride ions on the surface of the solid NaCl, as shown in Figure 14-2. Likewise, the δ^- parts of H_2O molecules (O atoms) orient themselves toward the Na^+ ions and solvate them. These attractions help to overcome the forces holding the ions in the crystal, and NaCl dissolves in the H_2O .



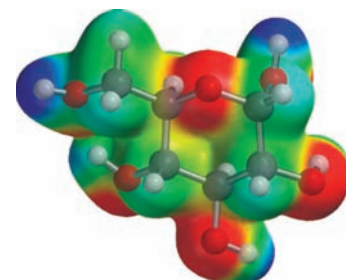
A The role of electrostatic attractions in the dissolution of NaCl in water. The δ^+ H of the polar H_2O molecule helps to attract Cl^- away from the crystal. Likewise, Na^+ is attracted by the δ^- O. Once they are separated from the crystal, both kinds of ions are surrounded by water molecules to complete the hydration process.



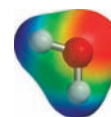
B Electrostatic plots illustrating the attraction of the positive portions (blue) of the water molecules to the negative ions, and the attraction of the negative portions (red) of the water molecules to the positive ions.



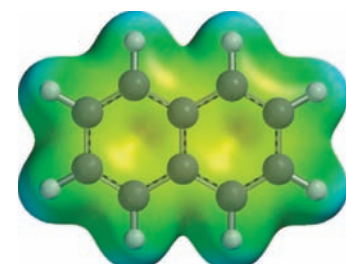
A cube of sugar is slowly dissolving, and the more dense sugar-rich solution can be seen descending through the less dense solvent.



Glucose, $C_6H_{12}O_6$



Water, H_2O



Naphthalene, $C_{10}H_8$

Glucose, like all sugars, is quite polar and dissolves in water, which is also very polar. Naphthalene is nonpolar and insoluble in water.

Figure 14-2 Interaction of water molecules with Na^+ cations and Cl^- anions

Unless otherwise noted, all content on this page is © Cengage Learning.



Solid ammonium nitrate, NH_4NO_3 , dissolves in water in a very endothermic process, absorbing heat from its surroundings. It is used in instant cold packs for early treatment of injuries, such as sprains and bruises, to minimize swelling.

STOP & THINK

The **charge density** (charge/radius ratio) of an ion is the ionic charge divided by the ionic radius in angstroms. Review the sizes of ions in Figure 5-4 carefully.

► For simplicity, we often omit the (aq) designations from dissolved ions. Remember that all ions are hydrated in aqueous solution, whether this is indicated or not.

► A negative value for heat of hydration indicates that heat is *released* during hydration.

Table 14-1 Ionic Radii, Charge/Radius Ratios, and Hydration Energies for Some Cations

Ion	Ionic Radius (Å)	Charge/Radius Ratio	Hydration Energy (kJ/mol)
K^+	1.52	0.66	−351
Na^+	1.16	0.86	−435
Li^+	0.90	1.11	−544
Ca^{2+}	1.14	1.75	−1650
Fe^{2+}	0.76	2.63	−1980
Zn^{2+}	0.74	2.70	−2100
Cu^{2+}	0.72	2.78	−2160
Fe^{3+}	0.64	4.69	−4340
Cr^{3+}	0.62	4.84	−4370
Al^{3+}	0.68	4.41	−4750

When we write $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$, we refer to hydrated ions. The number of H_2O molecules attached to an ion differs depending on the ion. Sodium ions are thought to be hexahydrated; that is, $\text{Na}^+(\text{aq})$ probably represents $[\text{Na}(\text{OH}_2)_6]^+$. Most cations in aqueous solution are surrounded by four to nine H_2O molecules, with six being the most common. Larger cations can generally accommodate more H_2O molecules than smaller cations.

Many solids that are appreciably soluble in water are ionic compounds. Magnitudes of crystal lattice energies generally increase with increasing charge and decreasing size of ions. That is, the size of the lattice energy increases as the ionic charge densities increase and, therefore, as the strength of electrostatic attractions within the crystal increases. Hydration energies vary in the same order (Table 14-1). As we indicated earlier, crystal lattice energies and hydration energies are generally much smaller in magnitude for molecular solids than for ionic solids.

Hydration and the effects of attractions in a crystal oppose each other in the dissolution process. Hydration energies and lattice energies are usually of about the same magnitude for low-charge species, so they often nearly cancel each other. As a result, the dissolution process is slightly endothermic for many ionic substances. Ammonium nitrate, NH_4NO_3 , is an example of a salt that dissolves endothermically. This property is used in the “instant cold packs” used to treat sprains and other minor injuries. Ammonium nitrate and water are packaged in a plastic bag in which they are kept separate by a partition that is easily broken when squeezed. As the NH_4NO_3 dissolves in the H_2O , the mixture absorbs heat from its surroundings and the bag becomes cold to the touch.

Many ionic solids dissolve with the release of heat. Examples are anhydrous sodium sulfate, Na_2SO_4 ; calcium acetate, $\text{Ca}(\text{CH}_3\text{COO})_2$; calcium chloride, CaCl_2 ; and lithium sulfate hydrate, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

As the charge-to-size ratio (charge density) increases for ions in ionic solids, the magnitude of the crystal lattice energy usually increases more than the hydration energy. This makes dissolution of solids that contain highly charged ions—such as aluminum fluoride, AlF_3 ; magnesium oxide, MgO ; and chromium(III) oxide, Cr_2O_3 —too endothermic to be soluble in water.

14-3 Dissolution of Liquids in Liquids (Miscibility)

The term **miscibility** is used to describe the ability of one liquid to dissolve in another. The three kinds of attractive interactions (solute–solute, solvent–solvent, and solvent–solute) must be considered for liquid–liquid solutions just as they were for solid–liquid solutions. Because solute–solute attractions are usually much weaker for liquid solutes than for solids, this factor is less important and so the mixing process is often exothermic for miscible liquids. Polar liquids tend to interact strongly with and dissolve readily in other polar liquids. Methanol, CH_3OH ; ethanol, $\text{CH}_3\text{CH}_2\text{OH}$; acetonitrile, CH_3CN ; and

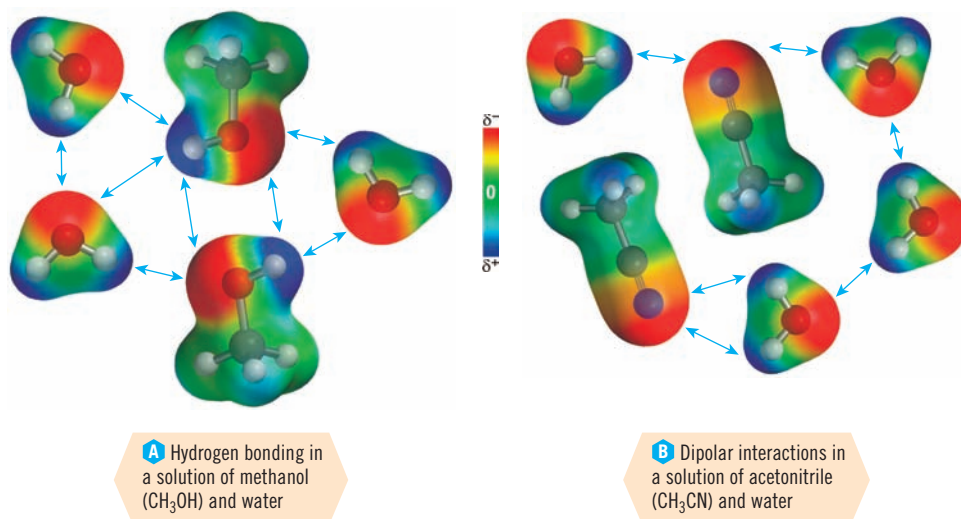


Figure 14-3 Molecules tend to arrange themselves to maximize attractions by bringing regions of opposite charge together while minimizing repulsions by separating regions of like charge. In this representation, colors for each molecule range from blue (most positive regions) to red (most negative regions).



The nonpolar molecules in oil do not attract polar water molecules, so oil and water are immiscible. The polar water molecules attract one another strongly—they “squeeze out” the nonpolar molecules in the oil. Oil is less dense than water, so it floats on water.

sulfuric acid, H_2SO_4 , are all polar liquids that are soluble in most polar solvents (such as water). The hydrogen bonding between methanol and water molecules and the dipolar interactions between acetonitrile and water molecules are depicted in Figure 14-3.

Because hydrogen bonding is so strong between sulfuric acid, H_2SO_4 , and water, a large amount of heat is released when concentrated H_2SO_4 is diluted with water (Figure 14-4). This can cause the solution to boil and spatter. If the major component of the mixture is water, this heat can be absorbed with less increase in temperature because of the unusually high specific heat of H_2O . For this reason, *sulfuric acid (as well as other concentrated mineral acids) must always be diluted by adding the acid slowly and carefully to water. Water should never be added to the acid.* Then if spattering did occur when the acid is added to water, it would be mainly water that spattered, not the corrosive concentrated acid that initially tends to sink to the bottom of the container.

Nonpolar liquids that do not react with the solvent generally are not very soluble in polar liquids because of the mismatch of forces of interaction. They are said to be *immiscible*. Nonpolar liquids are, however, usually quite soluble (*miscible*) in other nonpolar liquids. Between nonpolar molecules (whether alike or different) there are only dispersion forces, which are weak and easily overcome. As a result, when two nonpolar liquids are mixed, their molecules just “slide between” one another.

► Hydrogen bonding and dipolar interactions were discussed in Section 13-2.

► When water is added to concentrated acid, the danger is due more to the spattering of the acid itself than to the steam from boiling water.

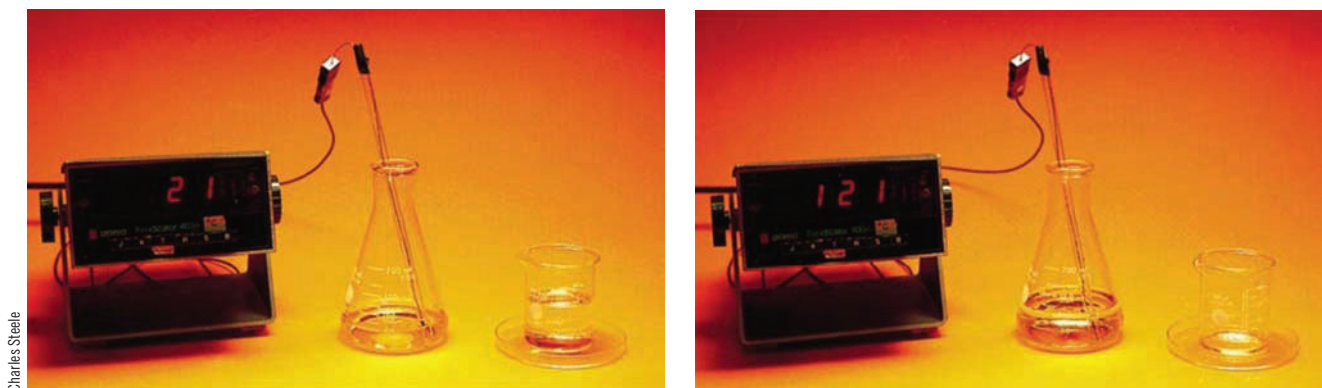
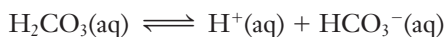
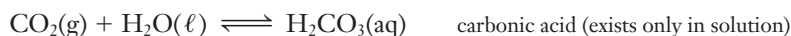


Figure 14-4 The heat released by pouring 50 mL of sulfuric acid, H_2SO_4 , into 50 mL of water increases the temperature by 100°C (from 21°C to 121°C)!

Unless otherwise noted, all content on this page is © Cengage Learning.

14-4 Dissolution of Gases in Liquids

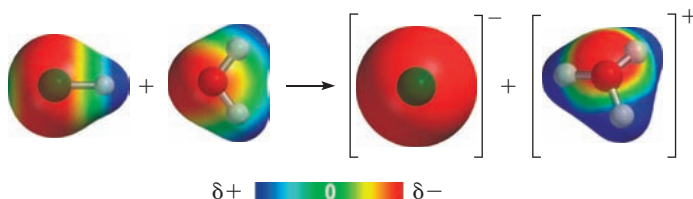
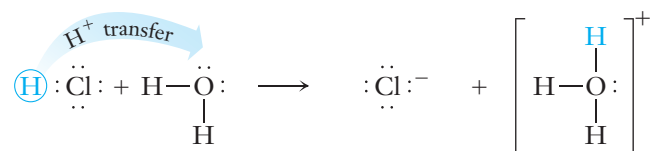
Based on Section 13-2 and the foregoing discussion, we should expect that polar gases are most soluble in polar solvents and nonpolar gases are most soluble in nonpolar liquids. Although carbon dioxide and oxygen are nonpolar gases, they do dissolve slightly in water. CO_2 is somewhat more soluble because it reacts with water to some extent to form carbonic acid, H_2CO_3 . This in turn ionizes slightly in two steps to give hydrogen ions, bicarbonate ions, and carbonate ions.



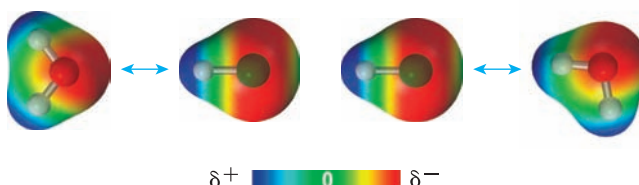
Approximately 1.45 grams of CO_2 (0.0329 mole) dissolves in a liter of water at 25°C and one atmosphere pressure.

Oxygen, O_2 , is less soluble than CO_2 in water, but it does dissolve to a noticeable extent due to dispersion forces (induced dipoles, Section 13-2). Only about 0.041 gram of O_2 (1.3×10^{-3} mole) dissolves in a liter of water at 25°C and 1 atm pressure. This is sufficient to support aquatic life.

The hydrogen halides, HF , HCl , HBr , and HI , are all polar covalent gases. In the gas phase the interactions among the widely separated molecules are not very strong, so solute-solute attractions are minimal. Due to the polarity of the hydrogen halides and the hydration of their ions, the dissolution processes in water are very exothermic. The resulting solutions, called hydrohalic acids, contain predominantly ionized HX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The ionization involves *protonation* of a water molecule by HX to form a hydrated hydrogen ion, H_3O^+ , and halide ion X^- (also hydrated).



HF is only slightly ionized in aqueous solution because of its strong covalent bond. In addition, the polar covalent bond between H and the small F atoms in HF causes very strong hydrogen bonding between H_2O and the largely intact HF molecules.



► Carbon dioxide is called an acid anhydride, that is, an “acid without water.” As noted in Section 5-9, many other oxides of nonmetals, such as N_2O_5 , SO_3 , and P_4O_{10} , are also acid anhydrides.



Charles Steele

Immersed in water, this green plant oxidizes the water to form gaseous oxygen. A small amount of the oxygen dissolves in water, and the excess oxygen forms bubbles of gas. The gaseous oxygen in the bubbles and the dissolved oxygen are in equilibrium with one another.

► Aqueous HCl , HBr , and HI are strong acids (Section 6-1, Part 2, and Section 10-7). Aqueous HF is a weak acid.



Charles Steele

A saturated solution of copper(II) sulfate, CuSO_4 , in water. As H_2O evaporates, blue $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals form. They are in dynamic equilibrium with the saturated solution.

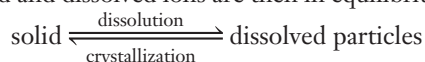
Unless otherwise noted, all content on this page is © Cengage Learning.

The only gases that dissolve appreciably in water are those that are capable of hydrogen bonding (such as HF), those that ionize extensively (such as HCl, HBr, and HI), and those that react with water (such as CO₂ or SO₃).

► Concentrated hydrochloric acid, HCl(aq), is an approximately 40% solution of HCl gas in water.

14-5 Rates of Dissolution and Saturation

At a given temperature, the rate of dissolution of a solid increases if large crystals are ground to a powder. Grinding increases the surface area, which in turn increases the number of solute ions or molecules in contact with the solvent. When a solid is placed in water, some of its particles solvate and dissolve. The rate of this process slows as time passes because the surface area of the crystals gets smaller and smaller. At the same time, the number of solute particles in solution increases, so they collide with the solid more frequently. Some of these collisions result in recrystallization. The rates of the two opposing processes become equal after some time. The solid and dissolved ions are then in equilibrium with each other.

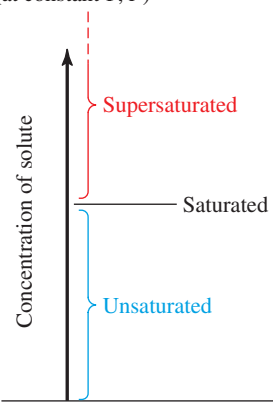


Such a solution is said to be **saturated**. Saturation occurs at very low concentrations of dissolved species for slightly soluble substances and at high concentrations for very soluble substances. When imperfect crystals are placed in saturated solutions of their ions, surface defects on the crystals are slowly “patched” with no net increase in mass of the solid. Often, after some time has passed, we see fewer but larger crystals. These observations provide evidence of the dynamic nature of the solubility equilibrium. When equilibrium is established, no more solid dissolves without the simultaneous crystallization of an equal mass of dissolved ions.

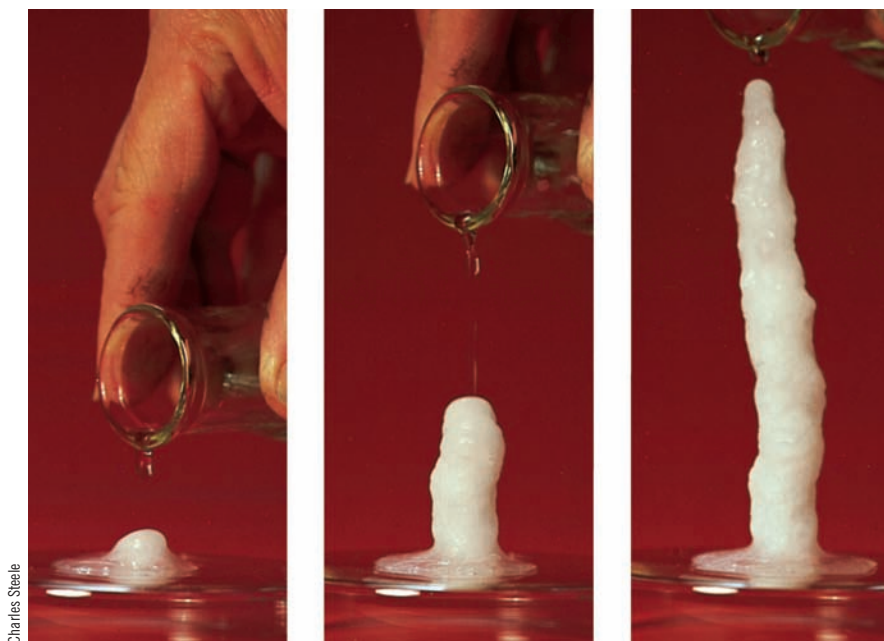
The solubilities of many solids increase at higher temperatures. **Supersaturated solutions** contain higher-than-saturated concentrations of solute. They can sometimes be prepared by saturating a solution at a high temperature. The saturated solution is then cooled slowly, without agitation, to a temperature at which the solute is less soluble. At this point, the resulting supersaturated solution is *metastable* (temporarily stable). This may be thought of as a state of pseudoequilibrium in which the system is at a higher energy than in its most stable state. In such a case, the solute has not yet become sufficiently organized for crystallization to begin. A supersaturated solution produces crystals rapidly if it is slightly disturbed or if it is “seeded” with a dust particle or a tiny crystal. Under such conditions enough solid crystallizes to leave a saturated solution (Figure 14-5).

► All saturated solutions involve dynamic equilibria; for instance, there is a continuous exchange of oxygen molecules across the surface of water in an open container. This allows fish to “breathe” dissolved oxygen.

(at constant T, P)

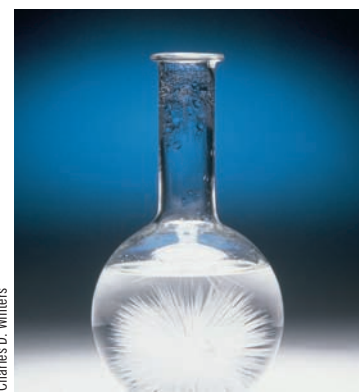


A solution that contains more than the amount of solute normally contained at saturation is said to be supersaturated. A solution that contains less than the amount of solute necessary for saturation is said to be unsaturated.



Charles Steele

Figure 14-5 A supersaturated solution can be seeded by pouring it very slowly onto a seed crystal. A supersaturated sodium acetate solution was used in these photographs.



Charles D. Winters

Sodium acetate crystals (NaCH₃COO) form quickly in a supersaturated solution when a small amount of solute is added.

Unless otherwise noted, all content on this page is © Cengage Learning.



Leon Lewandowski

Solid iodine, I_2 , dissolves to a limited extent in water to give an orange solution. This aqueous solution does not mix with nonpolar carbon tetrachloride, CCl_4 (left). After the funnel is shaken and the liquids are allowed to separate (right), the upper aqueous phase is lighter orange and the lower CCl_4 layer is much more highly colored. This is because iodine is much more soluble in the nonpolar carbon tetrachloride than in water; much of the iodine dissolves preferentially in the lower (CCl_4) phase. The design of the separatory funnel allows the lower (denser) layer to be drained off. Fresh CCl_4 could be added and the process repeated. This method of separation is called **extraction**. It takes advantage of the different solubilities of a solute in two immiscible liquids.



Charles Steele

Calcium acetate, $Ca(CH_3COO)_2$, is more soluble in cold water than in hot water. When a cold, concentrated solution of calcium acetate is heated, solid calcium acetate precipitates.

14-6 Effect of Temperature on Solubility

In Section 13-6 we introduced LeChatelier's Principle, which states that *when a stress is applied to a system at equilibrium, the system responds in a way that best relieves the stress*. Recall that exothermic processes release heat and endothermic processes absorb heat.

Exothermic: reactants $\longrightarrow$ products + **heat**

Endothermic: reactants + **heat** $\longrightarrow$ products

Many ionic solids dissolve by endothermic processes. Their solubilities in water usually *increase* as heat is added and the temperature increases. For example, KCl dissolves endothermically.

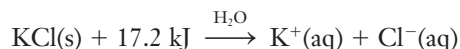


Figure 14-6 shows that the solubility of KCl increases as the temperature increases because more heat is available to increase the dissolving process. Raising the temperature (by adding *heat*) causes a stress on the solubility equilibrium. This stress favors the process that *absorbs* heat. In this case, more KCl dissolves.

Some solids, such as anhydrous Na_2SO_4 , and many liquids and gases dissolve by exothermic processes. Their solubilities usually decrease as temperature increases. The solubility of O_2 in water decreases (by 34%) from 0.041 gram per liter of water at $25^\circ C$ to 0.027 gram per liter at $50^\circ C$. Raising the temperature of rivers and lakes by dumping heated waste water from industrial plants and nuclear power plants is called **thermal pollution**. A slight increase in the temperature of the water causes a small but significant decrease in the concentration of dissolved oxygen. As a result, the water can no longer support the marine life it ordinarily could.

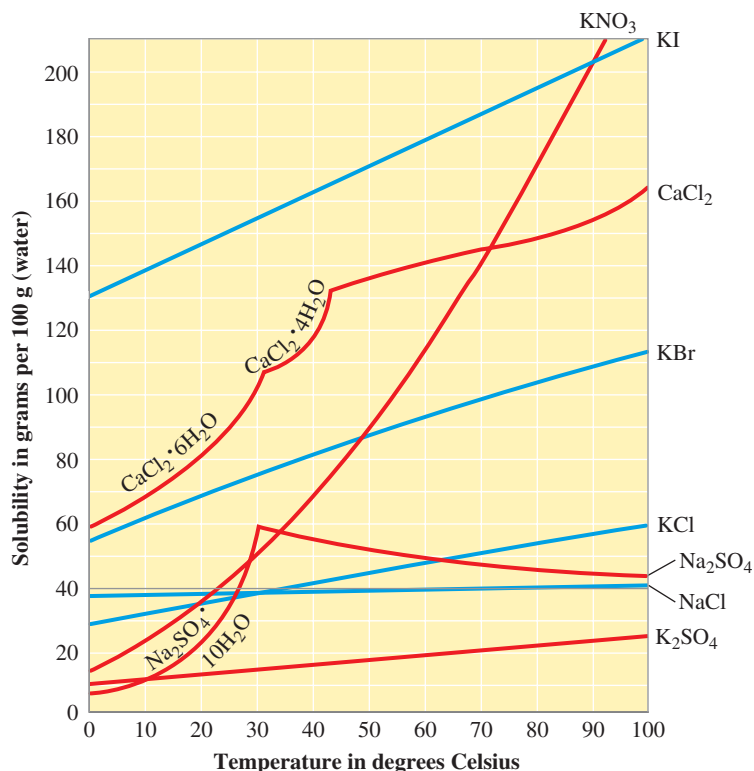
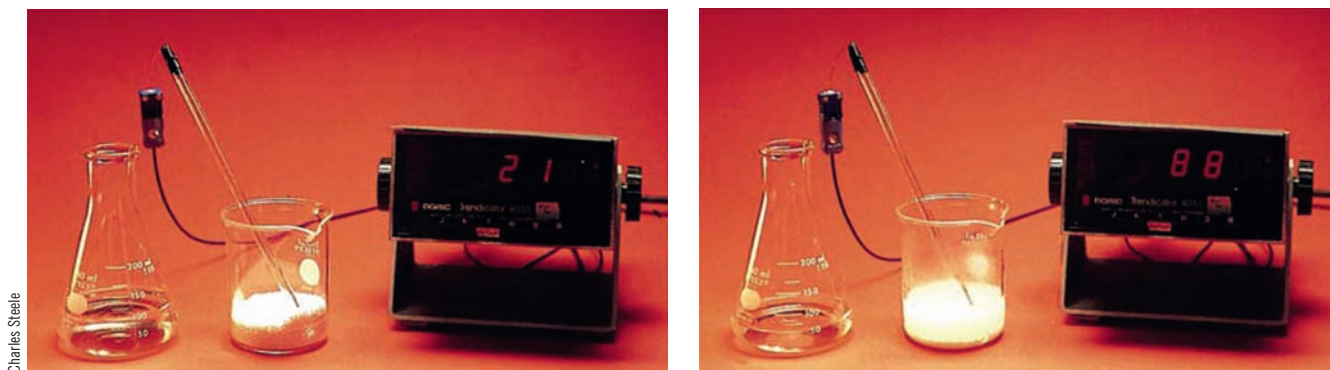


Figure 14-6 A graph that illustrates the effect of temperature on the solubilities of some salts. Some compounds exist either as nonhydrated crystalline substances or as hydrated crystals. Hydrated and nonhydrated crystal forms of the same compounds often have different solubilities because of the different total forces of attraction in the solids. The discontinuities in the solubility curves for $CaCl_2$ and Na_2SO_4 are due to transitions between hydrated and nonhydrated crystal forms.



The dissolution of anhydrous calcium chloride, CaCl_2 , in water is quite exothermic. Here the temperature increases from 21°C to 88°C. This dissolution process is utilized in commercial instant hot packs for quick treatment of injuries requiring heat.

14-7 Effect of Pressure on Solubility

Changing the pressure has no appreciable effect on the solubilities of either solids or liquids in liquids. The solubilities of gases in all solvents increase, however, as the partial pressures of the gases increase (Figure 14-7). Carbonated water is a saturated solution of carbon dioxide in water under pressure. When a can or bottle of a carbonated beverage is opened, the pressure on the surface of the beverage is reduced to atmospheric pressure, and much of the CO_2 bubbles out of solution. If the container is left open, the beverage becomes “flat” because the released CO_2 escapes.

Henry’s Law applies to gases that do not react with the solvent in which they dissolve (or, in some cases, gases that react incompletely). It is usually stated as follows.

The concentration or solubility of a gas in a liquid at any given temperature is directly proportional to the partial pressure of the gas over the solution.

$$C_{\text{gas}} = kP_{\text{gas}}$$

P_{gas} is the pressure of the gas above the solution, and k is a constant for a particular gas and solvent at a particular temperature. C_{gas} represents the concentration of dissolved gas; it is usually expressed either as molarity (see Section 3-6) or as mole fraction (see Section 14-8). The relationship is valid at low concentrations and low pressures.



Carbonated beverages can be used to illustrate Henry’s Law. When the bottle is opened, the equilibrium is disturbed and bubbles of CO_2 form within the liquid and rise to the surface. After some time, an equilibrium between dissolved CO_2 and atmospheric CO_2 is reached.

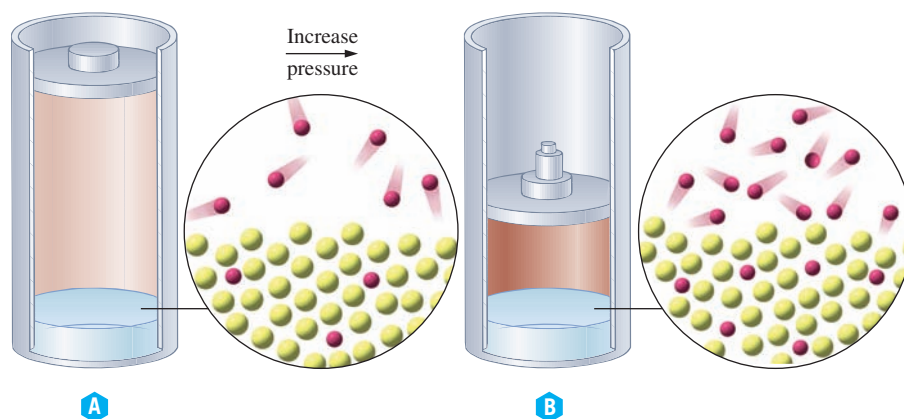


Figure 14-7 An illustration of Henry’s Law. The solubility of a gas (red) that does not react completely with the solvent (yellow) increases with increasing pressure of that gas above the solution.

Unless otherwise noted, all content on this page is © Cengage Learning.

14-8 Molality and Mole Fraction

We saw in Section 3-6 that concentrations of solutions are often expressed as percent by mass of solute or as molarity. Discussion of many physical properties of solutions is often made easier by expressing concentrations either in molality units or as mole fractions (Sections 14-9 to 14-14).

► Molality is based on the amount of *solvent*, not the amount of *solution*.

Molality

The **molality**, m , of a solute in solution is the number of moles of solute *per kilogram of solvent*.

$$\text{molality} = \frac{\text{number of moles solute}}{\text{number of kilograms solvent}}$$

Charles D. Winters



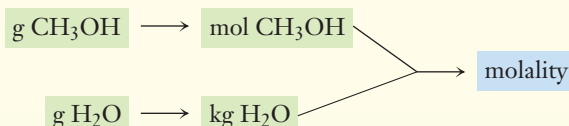
Each beaker holds the amount of a crystalline ionic compound that will dissolve in 100. grams of water at 100°C. The compounds are (left-most beaker, then clockwise): 102 grams of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, red-orange), 191 grams of cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, dark red), 341 grams of nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, green), 203 grams of copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, blue), 39 grams of sodium chloride (NaCl , white), and 79 grams of potassium chromate (K_2CrO_4 , yellow).

EXAMPLE 14-1 Molality

What is the molality of a solution that contains 54.6 g of CH_3OH in 108 g of water?

Plan

We convert the amount of solute (CH_3OH) to moles, express the amount of solvent (water) in kilograms, and apply the definition of molality.



Solution

$$\begin{aligned} \frac{? \text{ mol}}{\text{kg H}_2\text{O}} &= \frac{54.6 \text{ g CH}_3\text{OH}}{0.108 \text{ kg H}_2\text{O}} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.0 \text{ g CH}_3\text{OH}} = \frac{15.8 \text{ mol CH}_3\text{OH}}{\text{kg H}_2\text{O}} \\ &= 15.8 \text{ } m \text{ CH}_3\text{OH} \end{aligned}$$

You should now work Exercise 28.

EXAMPLE 14-2 Molality

How many grams of H_2O must be used to dissolve 50.0 grams of sucrose to prepare a 1.25 m solution of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$?

Plan

We convert the amount of solute ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) to moles, rearrange the molality expression for kilograms of solvent (water), and then express the result in grams.

Solution

$$\begin{aligned} ? \text{ mol C}_{12}\text{H}_{22}\text{O}_{11} &= 50.0 \text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}} = 0.146 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11} \\ \text{molality of solution} &= \frac{\text{mol C}_{12}\text{H}_{22}\text{O}_{11}}{\text{kg H}_2\text{O}} \end{aligned}$$

STOP & THINK

It is very easy to confuse molality (m) with molarity (M). Pay close attention to what is being asked.

Rearranging gives

$$\begin{aligned}\text{kg H}_2\text{O} &= \frac{\text{mol C}_{12}\text{H}_{22}\text{O}_{11}}{\text{molality of solution}} = \frac{0.146 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{1.25 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}/\text{kg H}_2\text{O}} \\ &= 0.117 \text{ kg H}_2\text{O} = 117 \text{ g H}_2\text{O}\end{aligned}$$

We will calculate several properties of this solution in other examples later in this chapter.

STOP & THINK

Use of complete unit factors will help you to solve problems involving solution concentrations in various required units.

Mole Fraction

Recall that in Chapter 12 the **mole fractions**, X_A and X_B , of each component in a mixture containing components A and B were defined as

$$X_A = \frac{\text{no. mol A}}{\text{no. mol A} + \text{no. mol B}} \quad \text{and} \quad X_B = \frac{\text{no. mol B}}{\text{no. mol A} + \text{no. mol B}}$$

Mole fraction is a dimensionless quantity; that is, it has no units.

EXAMPLE 14-3 Mole Fraction

What are the mole fractions of CH_3OH and H_2O in the solution described in Example 14-1? It contains 54.6 grams of CH_3OH and 108 grams of H_2O .

Plan

We express the amount of both components in moles, and then apply the definition of mole fraction.

Solution

$$\underline{\hspace{1cm}} \text{ mol CH}_3\text{OH} = 54.6 \text{ g CH}_3\text{OH} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.0 \text{ g CH}_3\text{OH}} = 1.71 \text{ mol CH}_3\text{OH}$$

$$\underline{\hspace{1cm}} \text{ mol H}_2\text{O} = 108 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} = 6.00 \text{ mol H}_2\text{O}$$

Now we calculate the mole fraction of each component.

$$X_{\text{CH}_3\text{OH}} = \frac{\text{no. mol CH}_3\text{OH}}{\text{no. mol CH}_3\text{OH} + \text{no. mol H}_2\text{O}} = \frac{1.71 \text{ mol}}{(1.71 + 6.00) \text{ mol}} = 0.222$$

$$X_{\text{H}_2\text{O}} = \frac{\text{no. mol H}_2\text{O}}{\text{no. mol CH}_3\text{OH} + \text{no. mol H}_2\text{O}} = \frac{6.00 \text{ mol}}{(1.71 + 6.00) \text{ mol}} = 0.778$$

You should now work Exercise 30.

STOP & THINK

Check: In any mixture the sum of the mole fractions must be 1:

$$0.222 + 0.778 = 1$$

Colligative Properties of Solutions

Physical properties of solutions that depend on the *number*, but not the *kind*, of solute particles in a given amount of solvent are called **colligative properties**. There are four important colligative properties of a solution that are directly proportional to the number of solute particles present. They are (1) vapor pressure lowering, (2) boiling point elevation, (3) freezing point depression, and (4) osmotic pressure. These properties of a solution depend on the *total concentration of all solute particles*, regardless of their ionic or molecular nature, charge, or size. For most of this chapter, we will consider *nonelectrolyte* solutes (see Section 6-1, Part 1); these substances dissolve to give one mole of dissolved particles for each mole of solute. In Section 14-14 we will see how we must adjust our predictions of colligative properties to account for ion formation in electrolyte solutions.

► *Colligative* means “tied together.”

14-9 Lowering of Vapor Pressure and Raoult's Law

Many experiments have shown that a solution containing a *nonvolatile* liquid or a solid as a solute always has a lower vapor pressure than the pure solvent (Figure 14-8). The vapor pressure of a liquid depends on the ease with which the molecules are able to escape from the surface of the liquid. When a solute is dissolved in a liquid, some of the total volume of the solution is occupied by solute molecules, so there are fewer solvent molecules *per unit area* at the surface. As a result, solvent molecules vaporize at a slower rate than if no solute were present. The increase in disorder that accompanies evaporation is also a significant factor. Because a solution is already more disordered (“mixed up”) than a pure solvent, the evaporation of the pure solvent involves a larger increase in disorder and is thus more favorable. Hence, the pure solvent exhibits a higher vapor pressure than does the solution. The lowering of the vapor pressure of the solution is a colligative property. It is a function of the number, and not the kind, of solute particles in solution. We emphasize that solutions of gases or low-boiling (volatile) liquid solutes can have *higher* total vapor pressures than the pure solvents, so this discussion does not apply to them.

The lowering of the vapor pressure of a solvent due to the presence of *nonvolatile, non-ionizing* solutes is summarized by **Raoult's Law**.

The vapor pressure of a solvent in an ideal solution is directly proportional to the mole fraction of the solvent in the solution.

The relationship can be expressed mathematically as

$$P_{\text{solvent}} = X_{\text{solvent}} P^0_{\text{solvent}}$$

where X_{solvent} represents the mole fraction of the solvent in a solution, P^0_{solvent} is the vapor pressure of the *pure* solvent, and P_{solvent} is the vapor pressure of the solvent *in the solution* (Figure 14-9). If the solute is nonvolatile, the vapor pressure of the solution is entirely due to the vapor pressure of the solvent, $P_{\text{solution}} = P_{\text{solvent}}$.

The *lowering* of the vapor pressure, $\Delta P_{\text{solvent}}$, is defined as

$$\Delta P_{\text{solvent}} = P^0_{\text{solvent}} - P_{\text{solvent}}$$

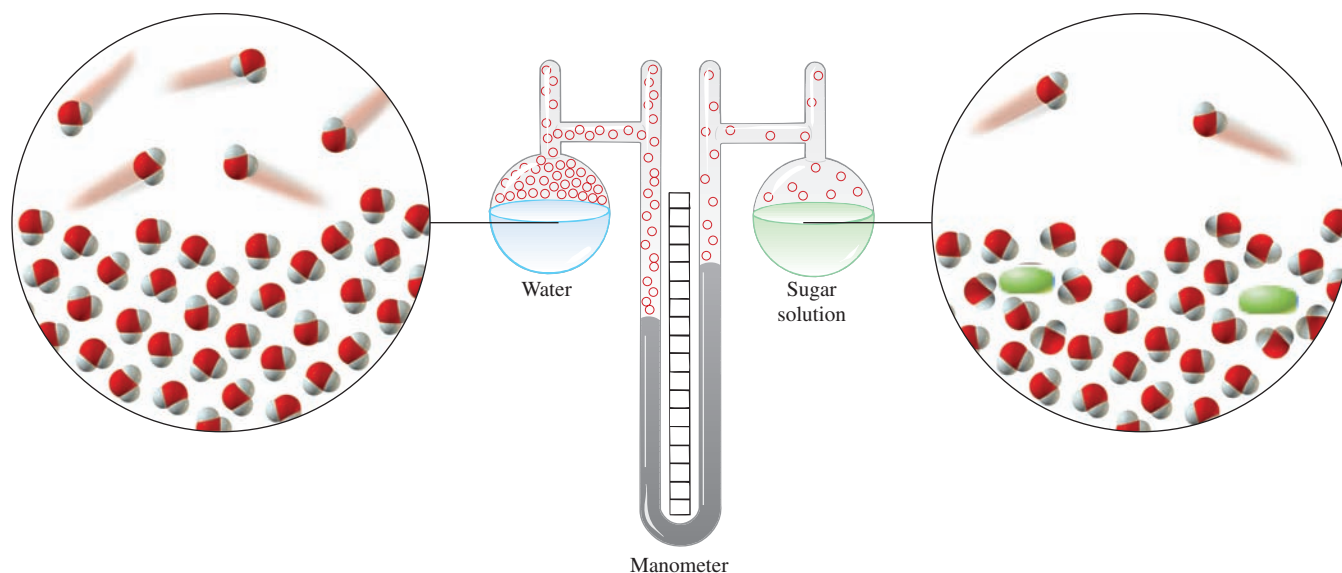


Figure 14-8 Lowering of vapor pressure. If no air is present in the apparatus, the pressure above each liquid is due to water vapor. This pressure is less over the solution of sugar and water.

► A *vapor* is a gas formed by the boiling or evaporation of a liquid or sublimation of a solid. The *vapor pressure* of a liquid is the pressure (partial pressure) exerted by a vapor in equilibrium with its liquid (see Section 13-7).

Thus,

$$\Delta P_{\text{solvent}} = P_{\text{solvent}}^0 - (X_{\text{solvent}} P_{\text{solvent}}^0) = (1 - X_{\text{solvent}}) P_{\text{solvent}}^0$$

Now $X_{\text{solvent}} + X_{\text{solute}} = 1$, so $1 - X_{\text{solvent}} = X_{\text{solute}}$. We can express the *lowering* of the vapor pressure in terms of the mole fraction of the solute.

$$\Delta P_{\text{solvent}} = X_{\text{solute}} P_{\text{solvent}}^0$$

Solutions that obey this relationship exactly are called **ideal solutions**. The vapor pressures of many solutions, however, do not behave ideally.

EXAMPLE 14-4 Vapor Pressure of a Solution of Nonvolatile Solute

Sucrose is a nonvolatile, nonionizing solute in water. Determine the vapor pressure lowering, at 25°C, of the 1.25 *m* sucrose solution in Example 14-2. Assume that the solution behaves ideally. The vapor pressure of pure water at 25°C is 23.8 torr (see Appendix E).

Plan

The solution in Example 14-2 was made by dissolving 50.0 grams of sucrose (0.146 mol) in 117 grams of water (6.50 mol). We calculate the mole fraction of the solute in the solution. Then we apply Raoult's Law to find the vapor pressure lowering, $\Delta P_{\text{solvent}}$.

Solution

$$X_{\text{sucrose}} = \frac{0.146 \text{ mol}}{0.146 \text{ mol} + 6.50 \text{ mol}} = 0.0220$$

Applying Raoult's Law in terms of the vapor pressure lowering,

$$\Delta P_{\text{solvent}} = (X_{\text{solute}})(P_{\text{solvent}}^0) = (0.0220)(23.8 \text{ torr}) = 0.524 \text{ torr}$$

You should now work Exercise 38.

When a solution consists of two components that are very similar, each component behaves essentially as it would if it were pure. For example, the two liquids heptane, C_7H_{16} , and octane, C_8H_{18} , are so similar that each heptane molecule experiences nearly the same intermolecular forces whether it is near another heptane molecule or near an octane molecule, and similarly for each octane molecule. The properties of such a solution can be predicted from a knowledge of its composition and the properties of each component. Such a solution is very nearly ideal.

Consider an ideal solution of two volatile components, A and B. The vapor pressure of each component above the solution is proportional to its mole fraction in the solution.

$$P_A = X_A P_A^0 \quad \text{and} \quad P_B = X_B P_B^0$$

According to Dalton's Law of Partial Pressures (see Section 12-11), the total vapor pressure of the solution is equal to the sum of the vapor pressures of the two components.

$$P_{\text{total}} = P_A + P_B \quad \text{or} \quad P_{\text{total}} = X_A P_A^0 + X_B P_B^0$$

This is shown graphically in Figure 14-10. We can use these relationships to predict the vapor pressures of an ideal solution, as Example 14-5 illustrates.

EXAMPLE 14-5 Vapor Pressure of a Solution of Volatile Components

At 40°C, the vapor pressure of pure heptane is 92.0 torr and the vapor pressure of pure octane is 31.0 torr. Consider a solution that contains 1.00 mole of heptane and 4.00 moles of octane. Calculate the vapor pressure of each component and the total vapor pressure above the solution.

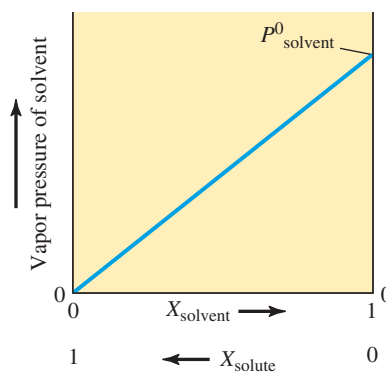


Figure 14-9 Raoult's Law for an ideal solution of a solute in a volatile liquid. The vapor pressure exerted by the liquid is proportional to its mole fraction in the solution.

STOP & THINK

The vapor pressure of water in the solution is $(23.8 - 0.524) \text{ torr} = 23.3 \text{ torr}$.

We could calculate this vapor pressure directly from the mole fraction of the solvent (water) in the solution, using the relationship

$$P_{\text{solvent}} = X_{\text{solvent}} P_{\text{solvent}}^0$$

► If component B were nonvolatile, then P_B^0 would be zero, and this description would be the same as that given earlier for a solution of a nonvolatile, nonionizing solute in a volatile solvent, $P_{\text{total}} = P_{\text{solvent}}$.

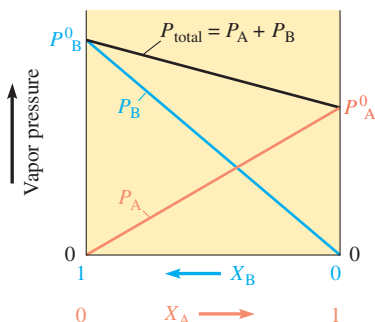


Figure 14-10 Raoult's Law for an ideal solution of two volatile components. The left-hand side of the plot corresponds to pure B ($X_A = 0$, $X_B = 1$), and the right-hand side corresponds to pure A ($X_A = 1$, $X_B = 0$). Of these hypothetical liquids, B is more volatile than A ($P_B^0 > P_A^0$).

STOP & THINK

Heptane (pure vapor pressure = 92.0 torr at 40°C) is a more volatile liquid than octane (pure vapor pressure = 31.0 torr at 40°C). Its mole fraction in the vapor, 0.426, is higher than its mole fraction in the liquid, 0.200.

Plan

We first calculate the mole fraction of each component in the liquid solution. Then we apply Raoult's Law to each of the two volatile components. The total vapor pressure is the sum of the vapor pressures of the components.

Solution

We first calculate the mole fraction of each component in the liquid solution.

$$X_{\text{heptane}} = \frac{1.00 \text{ mol heptane}}{(1.00 \text{ mol heptane}) + (4.00 \text{ mol octane})} = 0.200$$

$$X_{\text{octane}} = 1 - X_{\text{heptane}} = 0.800$$

Then, applying Raoult's Law for volatile components,

$$P_{\text{heptane}} = X_{\text{heptane}} P_{\text{heptane}}^0 = (0.200)(92.0 \text{ torr}) = 18.4 \text{ torr}$$

$$P_{\text{octane}} = X_{\text{octane}} P_{\text{octane}}^0 = (0.800)(31.0 \text{ torr}) = 24.8 \text{ torr}$$

$$P_{\text{total}} = P_{\text{heptane}} + P_{\text{octane}} = 18.4 \text{ torr} + 24.8 \text{ torr} = 43.2 \text{ torr}$$

You should now work Exercise 40.

The vapor in equilibrium with a liquid solution of two or more volatile components has a higher mole fraction of the more volatile component than does the liquid solution.

EXAMPLE 14-6 Composition of Vapor

Calculate the mole fractions of heptane and octane in the vapor that is in equilibrium with the solution in Example 14-5.

Plan

We learned in Section 12-11 that the mole fraction of a component in a gaseous mixture equals the ratio of its partial pressure to the total pressure. In Example 14-5 we calculated the partial pressure of each component in the vapor and the total vapor pressure.

Solution

In the *vapor*

$$X_{\text{heptane}} = \frac{P_{\text{heptane}}}{P_{\text{total}}} = \frac{18.4 \text{ torr}}{43.2 \text{ torr}} = 0.426$$

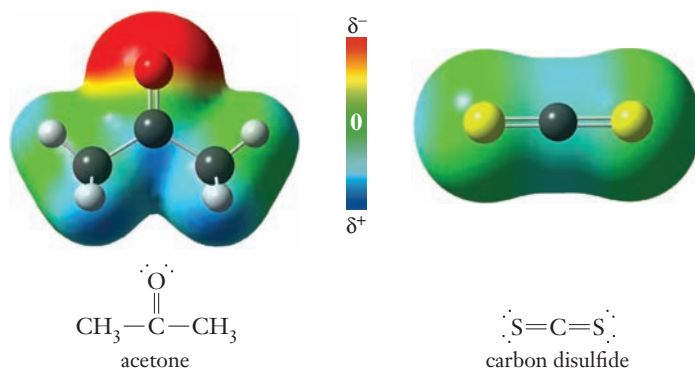
$$X_{\text{octane}} = \frac{P_{\text{octane}}}{P_{\text{total}}} = \frac{24.8 \text{ torr}}{43.2 \text{ torr}} = 0.574$$

or

$$X_{\text{octane}} = 1.000 - 0.426 = 0.574$$

You should now work Exercise 42.

Many dilute solutions behave ideally. Some solutions do not behave ideally over the entire concentration range. For some solutions, the observed vapor pressure is greater than that predicted by Raoult's Law (Figure 14-11a). This kind of deviation, known as a *positive deviation*, is due to differences in polarity of the two components. On the molecular level, the two substances do not mix entirely randomly, so there is self-association of each component with local regions enriched in one type of molecule or the other. In a region enriched in A molecules, substance A acts as though its mole fraction were greater than it is in the solution as a whole, and the vapor pressure due to A is greater than if the solution were ideal. A similar description applies to component B. The total vapor pressure is then greater than it would be if the solution were behaving ideally. A solution of acetone (polar) and carbon disulfide (nonpolar) is an example of a solution that shows a positive deviation from Raoult's Law.



Another, more common type of deviation occurs when the total vapor pressure is less than that predicted (Figure 14-11b). This is called a *negative deviation*. Such an effect is due to unusually strong attractions (such as hydrogen bonding) between *different polar* molecules. As a result, different polar molecules are strongly attracted to one another, so fewer molecules escape to the vapor phase. The observed vapor pressure of each component is thus less than ideally predicted. An acetone–chloroform solution and an ethanol–water solution are two polar combinations that show negative deviations from Raoult's Law.

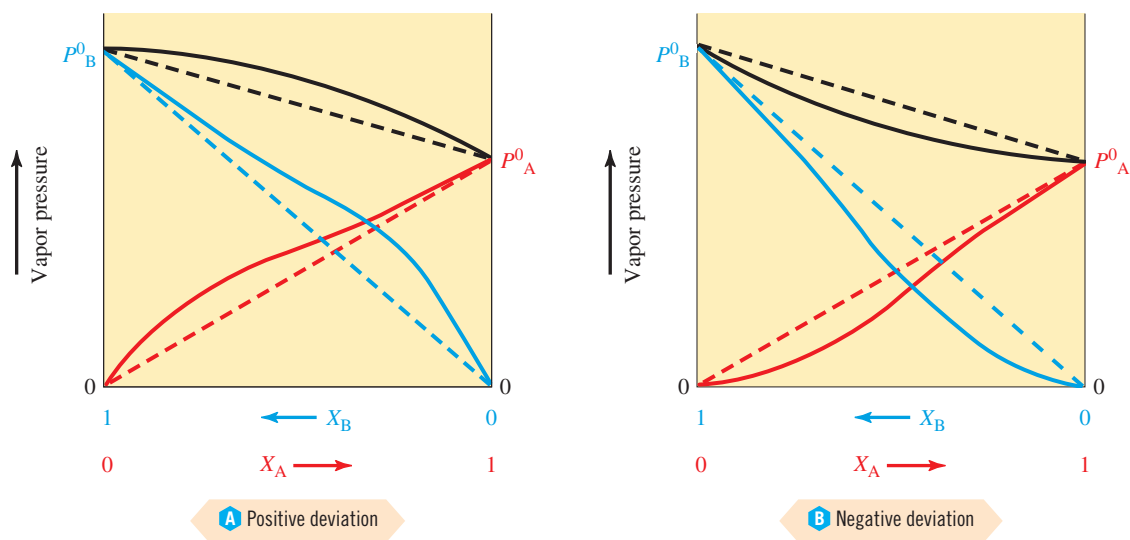
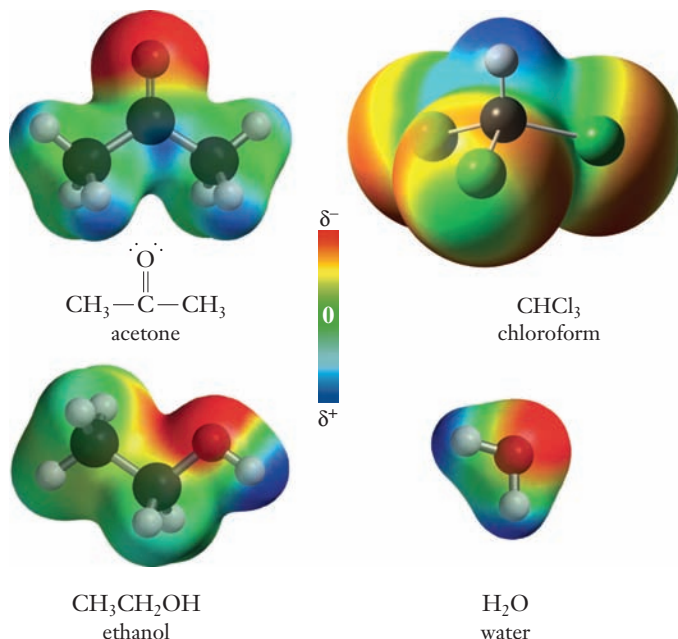


Figure 14-11
Deviations (solid lines) from Raoult's Law for two volatile components. Ideal behavior (Raoult's Law) is shown by the dashed lines.



14-10 Fractional Distillation

► The applied pressure is usually atmospheric pressure. Distillation under vacuum lowers the applied pressure. This allows boiling at lower temperatures than under atmospheric pressure. This technique allows distillation of some substances that would decompose at higher temperatures.

In Section 13-8 we described *simple* distillation as a process in which a liquid solution can be separated into volatile and nonvolatile components. But separation of volatile components is not very efficient by this method. Consider the simple distillation of a liquid solution consisting of two volatile components. If the temperature is slowly raised, the solution begins to boil when the sum of the vapor pressures of the components reaches the applied pressure on the surface of the solution. Both components exert vapor pressures, so both are carried away as a vapor and then condensed to form a liquid *distillate*. The resulting distillate is richer than the original liquid in the more volatile component (Example 14-6).

As a mixture of volatile liquids is distilled, the compositions of both the liquid and the vapor, as well as the boiling point of the solution, change continuously. At *constant pressure*, we can represent these quantities in a **boiling point diagram** (Figure 14-12). In such a diagram, the lower curve represents the boiling point of a *liquid mixture* with the indicated composition. The upper curve represents the composition of the *vapor* in equilibrium with the boiling liquid mixture at the indicated temperature. The intercepts at the two vertical axes show the boiling points of the two pure liquids. The distillation of the two liquids is described in the legend for Figure 14-12.

From the boiling point diagram in Figure 14-12, we see that two or more volatile liquids cannot be completely separated from each other by a single distillation step. The vapor collected at any boiling temperature is always enriched in the more volatile component (A); however, at any temperature the vapor still contains both components. A *series* of simple distillations would provide distillates increasingly richer in the more volatile component, but the repeated distillations would be very tedious.

Repeated distillations may be avoided by using **fractional distillation**. A *fractionating column* is inserted above the solution and attached to the condenser (Figure 14-13). The column is constructed so that it has a large surface area or is packed with many small glass beads or another material with a large surface area. These provide surfaces on which condensation can occur. Contact between the vapor and the packing favors condensation of the less vola-

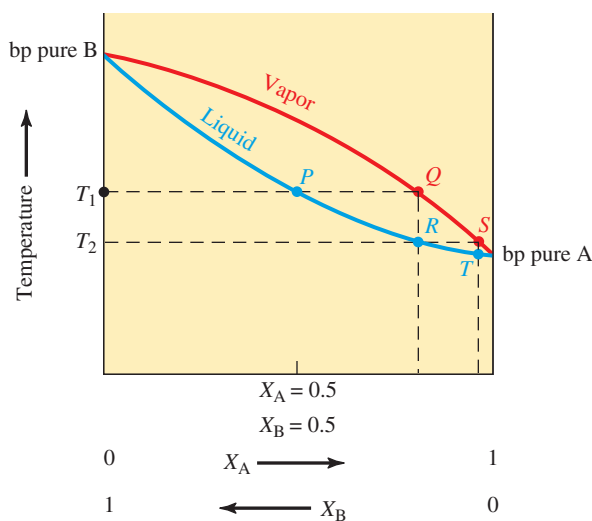
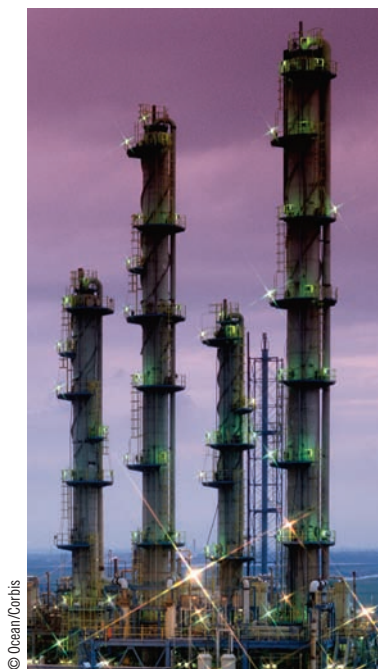


Figure 14-12 A boiling point diagram for a solution of two volatile liquids, A and B. The lower curve represents the boiling point of a liquid mixture with the indicated composition. The upper curve represents the composition of the *vapor* in equilibrium with the boiling liquid mixture at the indicated temperature. Pure liquid A boils at a lower temperature than pure liquid B; hence, A is the more volatile liquid in this illustration. Suppose we begin with an ideal equimolar mixture ($X_A = X_B = 0.5$) of liquids A and B. The point P represents the temperature at which this solution boils, T_1 . The vapor that is present at this equilibrium is indicated by point Q ($X_A \approx 0.8$). Condensation of that vapor at temperature T_2 gives a liquid of the same composition (point R). At this point we have described one step of simple distillation. The boiling liquid at point R is in equilibrium with the vapor of composition indicated by point S ($X_A > 0.95$), and so on.



Crude oil is separated by fractional distillation into many components such as gasoline, kerosene, fuel oil, paraffin, and asphalt. The distillation towers in chemical plants are typically four to ten stories tall and can process many tons of liquid mixtures each day.

Unless otherwise noted, all content on this page is © Cengage Learning.

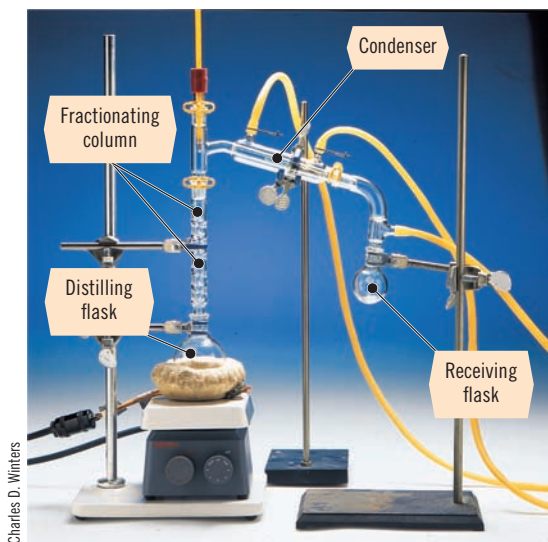


Figure 14-13 A fractional distillation apparatus. The vapor rising in the column is in equilibrium with the liquid that has condensed and is flowing slowly back down the column.

tile component. The column is cooler at the top than at the bottom. By the time the vapor reaches the top of the column, practically all of the less volatile component has condensed and fallen back down the column. The more volatile component goes into the condenser, where it is liquefied and delivered as a highly enriched distillate into the collection flask. The longer the column or the greater the packing, the more efficient is the separation.

14-11 Boiling Point Elevation

Recall that the boiling point of a liquid is the temperature at which its vapor pressure equals the applied pressure on its surface (see Section 13-8). For liquids in open containers, this is atmospheric pressure, and the temperature is the *normal boiling point*. We have seen that the vapor pressure of a solvent at a given temperature is lowered by the presence of a *nonvolatile* solute. Such a solution must then be heated to a higher temperature, $T_{b(\text{solution})}$, than that of the pure solvent T_b , to cause the vapor pressure of the solvent to equal atmospheric pressure (Figure 14-14). In accord with Raoult's Law, the elevation of

► When the solute is nonvolatile, only the *solvent* distills from the solution.

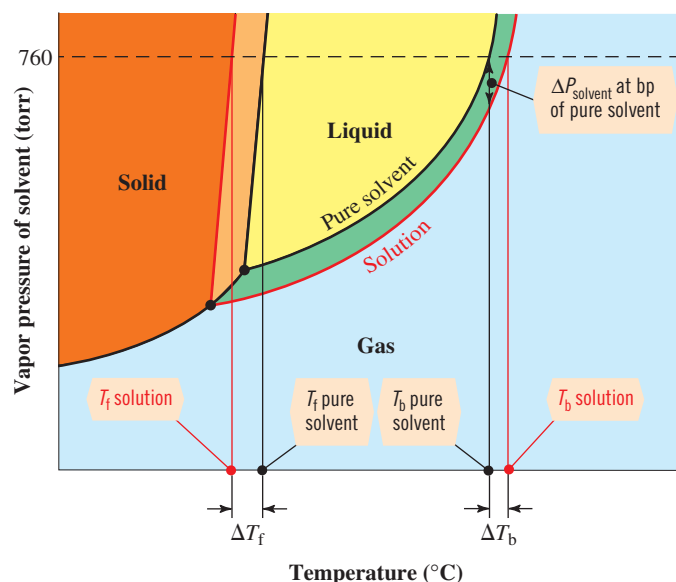


Figure 14-14 Because a *nonvolatile* solute lowers the vapor pressure of a solvent, the boiling point of a solution is higher and the freezing point lower than the corresponding points for the pure solvent. The boiling point elevation, ΔT_b , is positive, and its magnitude is less than the magnitude of the freezing point depression, ΔT_f .

Unless otherwise noted, all content on this page is © Cengage Learning.

STOP & THINK

$\Delta T_b = T_{b(\text{solution})} - T_{b(\text{pure solvent})}$. The boiling point of any solution that contains nonvolatile solutes is always higher than the boiling point of the pure solvent, so ΔT_b is always positive.

the boiling point of a solvent caused by the presence of a nonvolatile, nonionized solute is proportional to the number of moles of solute dissolved in a given mass of solvent. Mathematically, the boiling point elevation is expressed as

$$\Delta T_b = K_b m$$

The term ΔT_b represents the elevation of the boiling point of the solvent, that is, the boiling point of the solution minus the boiling point of the pure solvent. The m is the molality of the *solute*, and K_b is a proportionality constant called the molal **boiling point elevation constant**. This constant is different for different solvents and *does not* depend on the solute (Table 14-2).

Table 14-2 Some Properties of Common Solvents

Solvent	bp (pure)	K_b ($^{\circ}\text{C}/m$)	fp (pure)	K_f ($^{\circ}\text{C}/m$)
water	100*	0.512	0*	1.86
benzene	80.1	2.53	5.5	5.12
acetic acid	118.1	3.07	16.6	3.90
nitrobenzene	210.9	5.24	5.7	7.00
phenol	182	3.56	43	7.40
camphor	207.4	5.61	178.4	40.0

*Exact values by definition.

K_b corresponds to the change in boiling point produced by a one-molal *ideal* solution of a nonvolatile nonelectrolyte. The units of K_b are $^{\circ}\text{C}/m$.

Elevations of boiling points are usually quite small for solutions of typical concentrations. They can be measured, however, with specially constructed differential thermometers that measure small temperature changes accurately to the nearest 0.001°C .

EXAMPLE 14-7 Boiling Point Elevation

Predict the boiling point of the 1.25 m sucrose solution in Example 14-2. Sucrose is a nonvolatile, nonionized solute.

Plan

We first find the *increase* in boiling point from the relationship $\Delta T_b = K_b m$. The boiling point is *higher* by this amount than the normal boiling point of pure water.

Solution

From Table 14-2, K_b for $\text{H}_2\text{O} = 0.512^{\circ}\text{C}/m$, so

$$\Delta T_b = (0.512^{\circ}\text{C}/m)(1.25\ m) = 0.640^{\circ}\text{C}$$

The solution would boil at a temperature that is 0.640°C higher than pure water would boil. The normal boiling point of pure water is exactly 100°C , so at 1.00 atm this solution is predicted to boil at $100^{\circ}\text{C} + 0.640^{\circ}\text{C} = 100.640^{\circ}\text{C}$.

You should now work Exercise 46.

STOP & THINK

Boiling point changes are usually small and always increase the boiling point, so this answer makes sense.

14-12 Freezing Point Depression

Molecules of liquids move more slowly and approach one another more closely as the temperature is lowered. The freezing point of a liquid is the temperature at which the forces of attraction among molecules are just great enough to overcome their kinetic energies and thus cause a phase change from the liquid to the solid state. Strictly speaking, the freezing (melting) point of a substance is the temperature at which the liquid and solid phases are in equilibrium. When a dilute solution freezes, it is the *solvent* that begins to solidify first, leaving the solute in a more concentrated solution. Solvent molecules are somewhat more separated in a solution from one another (because of solute particles) than they are in the pure solvent. Consequently, the temperature of a solution must be lowered below the freezing point of the pure solvent to freeze it.

The freezing point depression, $\Delta T_f = T_{f(\text{pure solvent})} - T_{f(\text{solution})}$, of any solution of nonelectrolytes has been found to be equal to the molality of the solute times a proportionality constant called the molal **freezing point depression constant**, K_f .

$$\Delta T_f = K_f m$$

The values of K_f for a few solvents are given in Table 14-2. Each is numerically equal to the freezing point depression of a one-molal *ideal* solution of a nonelectrolyte in that solvent.

EXAMPLE 14-8 Freezing Point Depression

When 15.0 grams of ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, is dissolved in 750. grams of formic acid, the freezing point of the solution is 7.20°C . The freezing point of pure formic acid is 8.40°C . Evaluate K_f for formic acid.

Plan

The molality and the depression of the freezing point are calculated first. Then we solve the equation $\Delta T_f = K_f m$ for K_f and substitute values for m and ΔT_f .

$$K_f = \frac{\Delta T_f}{m}$$

Solution

$$\text{molality} = \frac{\text{mol C}_2\text{H}_5\text{OH}}{\text{kg formic acid}} = \frac{15.0 \text{ g C}_2\text{H}_5\text{OH}}{0.750 \text{ kg formic acid}} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.0 \text{ g C}_2\text{H}_5\text{OH}} = 0.435 \text{ } m$$

$$\Delta T_f = (T_{f[\text{formic acid}]}) - (T_{f[\text{solution}]}) = 8.40^\circ\text{C} - 7.20^\circ\text{C} = 1.20^\circ\text{C} \quad (\text{depression})$$

$$\text{Then } K_f = \frac{\Delta T_f}{m} = \frac{1.20^\circ\text{C}}{0.435 \text{ } m} = 2.76^\circ\text{C}/m \text{ for formic acid.}$$

You should now work Exercise 48.

EXAMPLE 14-9 Freezing Point Depression

Calculate the freezing point of the $1.25 \text{ } m$ sucrose solution in Example 14-2.

Plan

We first find the *decrease* in freezing point from the relationship $\Delta T_f = K_f m$. The temperature at which the solution freezes is *lower* than the freezing point of pure water by this amount.

Solution

From Table 14-2, K_f for $\text{H}_2\text{O} = 1.86^\circ\text{C}/m$, so

$$\Delta T_f = (1.86^\circ\text{C}/m)(1.25 \text{ } m) = 2.32^\circ\text{C}$$



Charles D. Winters

When a solution freezes, the solvent solidifies as the pure substance. For this photo a dye has been added. As the solute freezes along the wall of the test tube, the dye concentration increases near the center.

STOP & THINK

ΔT_f is the *depression* of the freezing point. It is defined as

$$\Delta T_f = T_{f(\text{pure solvent})} - T_{f(\text{solution})}$$

so it is always *positive*.

STOP & THINK

Remember to use molality (m) and not molarity (M) when calculating boiling point elevation or freezing point depression.



James Hardy/Getty Images

Lime, CaO , is added to molten iron ore during the manufacture of pig iron. It lowers the melting point of the mixture. The metallurgy of iron is discussed in more detail in Chapter 26.

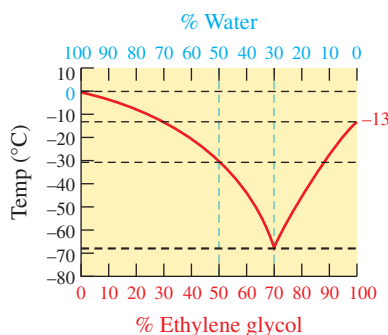
Unless otherwise noted, all content on this page is © Cengage Learning.

The solution freezes at a temperature 2.32°C below the freezing point of pure water, or

$$T_{\text{f(solution)}} = 0.00^{\circ}\text{C} - 2.32^{\circ}\text{C} = -2.32^{\circ}\text{C}$$

You should now work Exercise 56.

► The total concentration of all dissolved solute species determines the colligative properties. As we will emphasize in Section 14-14, we must take into account the extent of ion formation in solutions of ionic solutes.



Freezing point depression curve for water and ethylene glycol calculated from the $\Delta T_f = K_f m$ formula. Despite some differences due to nonideal behavior, it matches the experimental data fairly well.



Charles D. Winters

Ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, is the major component of “permanent” antifreeze. It depresses the freezing point of water in an automobile radiator and also raises its boiling point. The solution remains in the liquid phase over a wider temperature range than does pure water. This protects against both freezing and boil-over.

You may be familiar with several examples of the effects we have studied. Seawater does not freeze on some days when fresh water does, because seawater contains higher concentrations of solutes, mostly ionic solutes. Spreading soluble salts such as sodium chloride, NaCl , or calcium chloride, CaCl_2 , on an icy road lowers the freezing point of the ice, causing the ice to melt.

A familiar application is the addition of “permanent” antifreeze, mostly ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, to the water in an automobile radiator. Because the boiling point of the solution is elevated, addition of a solute as a winter antifreeze also helps protect against loss of the coolant by summer “boil-over.” The amounts by which the freezing and boiling points change depend on the concentration of the ethylene glycol solution. The addition of too much ethylene glycol is counterproductive, however. The freezing point of pure ethylene glycol is -13°C . A solution that is mostly ethylene glycol would have a somewhat lower freezing point due to the presence of water as a solute. Suppose you graph the freezing point depression of water below 0°C as ethylene glycol is added, and also graph the freezing point depression of ethylene glycol below -13°C as water is added. These two curves would intersect at some temperature, indicating the limit of lowering that can occur. Most antifreeze labels recommend a 50:50 mixture by volume (fp = -34°F , bp = 265°F with a 15-psi pressure cap on the radiator), and cite the limit of possible protection with a 70:30 mixture by volume of antifreeze:water (fp = -84°F , bp = 276°F with a 15-psi pressure cap).

14-13 Determination of Molecular Weight by Freezing Point Depression or Boiling Point Elevation

The colligative properties of freezing point depression and, to a lesser extent, boiling point elevation are useful in the determination of molecular weights of solutes. The solutes *must* be nonvolatile in the temperature range of the investigation if boiling point elevations are to be determined. We will restrict our discussion of determination of molecular weight to nonelectrolytes.

EXAMPLE 14-10 Molecular Weight from a Colligative Property

A 1.20-gram sample of an unknown covalent compound is dissolved in 50.0 grams of benzene. The solution freezes at 4.92°C . Calculate the molecular weight of the compound.

Plan

To calculate the molecular weight of the unknown compound, we find the number of moles that is represented by the 1.20 grams of unknown compound. We first use the freezing point data to find the molality of the solution. The molality relates the number of moles of solute to the mass of solvent (known), so this allows us to calculate the number of moles of the unknown compound.

Solution

From Table 14-2, the freezing point of pure benzene is 5.48°C and K_f is $5.12^{\circ}\text{C}/m$.

$$\Delta T_f = T_{\text{f(pure benzene)}} - T_{\text{f(solution)}} = 5.48^{\circ}\text{C} - 4.92^{\circ}\text{C} = 0.56^{\circ}\text{C}$$

$$m = \frac{\Delta T_f}{K_f} = \frac{0.56^{\circ}\text{C}}{5.12^{\circ}\text{C}/m} = 0.11 m$$

The molality is the number of moles of solute per kilogram of benzene, so the number of moles of solute in 50.0 g (0.0500 kg) of benzene can be calculated.

$$0.11 \, m = \frac{? \, \text{mol solute}}{0.0500 \, \text{kg benzene}}$$

$$? \, \text{mol solute} = (0.11 \, m)(0.0500 \, \text{kg}) = 0.0055 \, \text{mol solute}$$

$$\text{mass of 1.0 mol} = \frac{\text{no. of g solute}}{\text{no. of mol solute}} = \frac{1.20 \, \text{g solute}}{0.0055 \, \text{mol solute}} = 2.2 \times 10^2 \, \text{g/mol}$$

$$\text{molecular weight} = 2.2 \times 10^2 \, \text{amu}$$

You should now work Exercise 61.

EXAMPLE 14-11 Molecular Weight from a Colligative Property

Either camphor ($\text{C}_{10}\text{H}_{16}\text{O}$, molecular weight = 152 g/mol) or naphthalene (C_{10}H_8 , molecular weight = 128 g/mol) can be used to make mothballs. A 5.2-gram sample of mothballs was dissolved in 100. grams of ethanol, and the resulting solution had a boiling point of 78.90°C. Were the mothballs made of camphor or naphthalene? Pure ethanol has a boiling point of 78.41°C; its $K_b = 1.22^\circ\text{C}/m$.

Plan

We can distinguish between the two possibilities by determining the molecular weight of the unknown solute. We do this by the method shown in Example 14-10, except that now we use the observed boiling point data.

Solution

The observed boiling point elevation is

$$\Delta T_b = T_{b(\text{solution})} - T_{b(\text{solvent})} = (78.90 - 78.41)^\circ\text{C} = 0.49^\circ\text{C}$$

Using $\Delta T_b = 0.49^\circ\text{C}$ and $K_b = 1.22^\circ\text{C}/m$, we can find the molality of the solution.

$$\text{molality} = \frac{\Delta T_b}{K_b} = \frac{0.49^\circ\text{C}}{1.22^\circ\text{C}/m} = 0.40 \, m$$

The number of moles of solute in the 100. g (0.100 kg) of solvent used is

$$\left(0.40 \frac{\text{mol solute}}{\text{kg solvent}}\right)(0.100 \, \text{kg solvent}) = 0.040 \, \text{mol solute}$$

The molecular weight of the solute is its mass divided by the number of moles.

$$\frac{? \, \text{g}}{\text{mol}} = \frac{5.2 \, \text{g}}{0.040 \, \text{mol}} = 130 \, \text{g/mol}$$

The value 130 g/mol for the molecular weight indicates that **naphthalene** was used to make these mothballs.

You should now work Exercise 59.

STOP & THINK

Remember that grams of *solvent* must be converted into kg when using molalities (m).

14-14 Colligative Properties and Dissociation of Electrolytes

As we have emphasized, colligative properties depend on the *number* of solute particles in a given mass of solvent. A 0.100 molal *aqueous* solution of a covalent compound that does not ionize gives a freezing point depression of 0.186°C. If dissociation were complete, 0.100 m NaCl would have a *total* molality of 0.200 m (i.e., 0.100 m Na^+ + 0.100 m Cl^-). So we might predict that a 0.100 molal solution of this 1:1 strong electrolyte would have a

$$\begin{aligned} \Delta T_f &= K_f m \\ &= (1.86^\circ\text{C}/m)(0.100 \, m) \\ &= 0.186^\circ\text{C} \end{aligned}$$

Unless otherwise noted, all content on this page is © Cengage Learning.

freezing point depression of $2 \times 0.186^\circ\text{C}$, or 0.372°C . In fact, the *observed* depression is only 0.348°C . This value for ΔT_f is about 6% less than we would expect for an effective molality of $0.200\text{ }m$.

In an ionic solution the solute particles are not randomly distributed. Rather, each positive ion has more negative than positive ions near it. Some of the ions undergo **association** in solution (Figure 14-15). At any given instant, some Na^+ and Cl^- ions collide and “stick together.” During the brief time that they are in contact, they behave as a single particle. This tends to reduce the effective molality, causing the solution to behave non-ideally. The freezing point depression (ΔT_f) is therefore reduced (as well as the boiling point elevation (ΔT_b) and the lowering of vapor pressure).

► Ionic solutions are elegantly described by the Debye–Hückel theory, which is beyond the scope of this text.

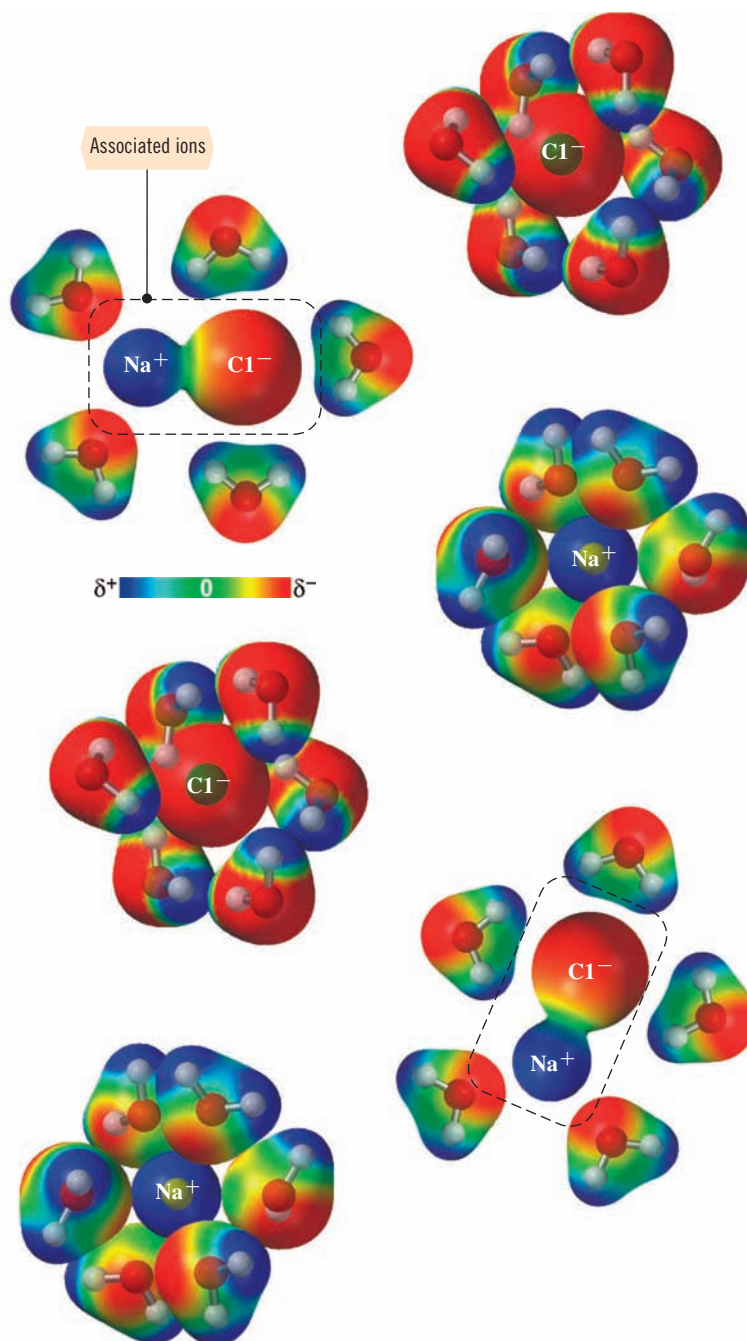


Figure 14-15 Diagrammatic representation of the various species thought to be present in a solution of NaCl in water. This would explain unexpected values for its colligative properties, such as freezing point depression.

A (more concentrated) 1.00 *m* solution of NaCl might be expected to have a freezing point depression of $2 \times 1.86^\circ\text{C} = 3.72^\circ\text{C}$, but the observed depression is only 3.40°C . This value for ΔT_f is about 9% less than we would expect for complete dissociation. We see a greater deviation from the depression predicted for an ideal solution in the more concentrated solution. This is because the Na^+ cations and Cl^- anions are closer together and collide more often in the more concentrated solution. Consequently, the ionic association is greater.

One measure of the extent of dissociation (or ionization) of an electrolyte in water is the **van't Hoff factor**, i , for the solution. This is the ratio of the *actual* colligative property to the value that *would* be observed *if no ionic dissociation occurred*.

$$i = \frac{\Delta T_{f(\text{actual})}}{\Delta T_{f(\text{if nonelectrolyte})}} = \frac{K_f m_{\text{effective}}}{K_f m_{\text{stated}}} = \frac{m_{\text{effective}}}{m_{\text{stated}}}$$

The ideal, or limiting, value of i for a solution of NaCl would be 2, and the value for a 2:1 electrolyte such as Na_2SO_4 would be 3; these values would apply to infinitely dilute solutions in which no appreciable ion association occurs. For 0.10 *m* and 1.0 *m* solutions of NaCl, i is somewhat *less than* 2.

$$\text{For } 0.10 \text{ } m: \quad i = \frac{0.348^\circ\text{C}}{0.186^\circ\text{C}} = 1.87 \quad \text{For } 1.0 \text{ } m: \quad i = \frac{3.40^\circ\text{C}}{1.86^\circ\text{C}} = 1.83$$

Table 14-3 lists actual and ideal values of i for solutions of some strong electrolytes, based on measurements of freezing point depressions.

Many weak electrolytes are quite soluble in water, but they ionize only slightly. The i value and percent ionization for a weak electrolyte in solution can also be determined from freezing point depression data (Example 14-12).

► Weak acids and weak bases (see Section 6-1) are weak electrolytes.

Table 14-3 Actual and Ideal van't Hoff Factors, i , for Aqueous Solutions of Nonelectrolytes and Strong Electrolytes

Compound	i for 0.100 <i>m</i> Solution	i for 1.00 <i>m</i> Solution
<i>nonelectrolytes</i>		
sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$	1.00 (ideal) 1.00	1.00 (ideal) 1.00
<i>If 2 ions in solution/formula unit</i>	2.00 (ideal)	2.00 (ideal)
KBr	1.88	1.77
NaCl	1.87	1.83
<i>If 3 ions in solution/formula unit</i>	3.00 (ideal)	3.00 (ideal)
K_2CO_3	2.45	2.39
K_2CrO_4	2.39	1.95
<i>If 4 ions in solution/formula unit</i>	4.00 (ideal)	4.00 (ideal)
$\text{K}_3[\text{Fe}(\text{CN})_6]$	2.85	—

EXAMPLE 14-12 Colligative Property and Weak Electrolytes

Lactic acid, $\text{C}_2\text{H}_4(\text{OH})\text{COOH}$, is found in sour milk. It is also formed in muscles during intense physical activity and is responsible for the pain felt during strenuous exercise. It is a weak monoprotic acid and therefore a weak electrolyte. The freezing point of a 0.0100 *m* aqueous solution of lactic acid is -0.0206°C . Calculate (a) the van't Hoff factor i and (b) the percent ionization in the solution.

Plan for (a)

To evaluate the van't Hoff factor, i , we first calculate $m_{\text{effective}}$ from the observed freezing point depression and K_f for water; we then compare $m_{\text{effective}}$ and m_{stated} to find i .



Lactic acid that is formed in muscles is responsible for the discomfort felt during strenuous physical activity.

Unless otherwise noted, all content on this page is © Cengage Learning.

Solution for (a)

$$m_{\text{effective}} = \frac{\Delta T_f}{K_f} = \frac{0.0206^\circ\text{C}}{1.86^\circ\text{C}/m} = 0.0111\ m$$

$$i = \frac{m_{\text{effective}}}{m_{\text{stated}}} = \frac{0.0111\ m}{0.0100\ m} = 1.11$$

Plan for (b)

The percent ionization is given by

$$\% \text{ ionization} = \frac{m_{\text{ionized}}}{m_{\text{original}}} \times 100\% \quad (\text{where } m_{\text{original}} = m_{\text{stated}} = 0.0100\ m)$$

The freezing point depression is caused by the $m_{\text{effective}}$, the total *concentration of all dissolved species*—in this case, the sum of the concentrations of HA, H^+ , and A^- . We know the value of $m_{\text{effective}}$ from part (a). Thus, we need to construct an expression for the effective molality in terms of the amount of lactic acid that ionizes. We represent the molality of lactic acid that ionizes as an unknown, x , and write the concentrations of all species in terms of this unknown.

Solution for (b)

In many calculations, it is helpful to write down (1) the values, or symbols for the values, of initial concentrations; (2) the changes in concentrations due to reaction; and (3) the final concentrations, as shown here. The coefficients of the equation are all ones, so the reaction ratio must be 1:1:1.

Let x = molality of lactic acid that ionizes; then

x = molality of H^+ and lactate ions that have been formed

	HA	→	H ⁺	+	A ⁻
Start	0.0100 <i>m</i>		0		0
Change	- <i>x m</i>		+ <i>x m</i>		+ <i>x m</i>
Final	(0.0100 - <i>x</i>) <i>m</i>		<i>x m</i>		<i>x m</i>

The $m_{\text{effective}}$ is equal to the sum of the molalities of all the solute particles.

$$\begin{aligned} m_{\text{effective}} &= m_{\text{HA}} + m_{\text{H}^+} + m_{\text{A}^-} \\ &= (0.0100 - x)\ m + x\ m + x\ m \\ &= (0.0100 + x)\ m \end{aligned}$$

This must equal the value for $m_{\text{effective}}$ calculated earlier, 0.0111 *m*.

$$0.0111\ m = (0.0100 + x)\ m$$

$$x = 0.0011\ m = \text{molality of the acid that ionizes}$$

We can now calculate the percent ionization.

$$\% \text{ ionization} = \frac{m_{\text{ionized}}}{m_{\text{original}}} \times 100\% = \frac{0.0011\ m}{0.0100\ m} \times 100\% = 11\%$$

This experiment shows that in 0.0100 *m* solutions, only 11% of the lactic acid has been converted into H^+ and $\text{C}_2\text{H}_4(\text{OH})\text{COO}^-$ ions. The remainder, 89%, exists as nonionized molecules.

You should now work Exercises 78 and 80.

► To simplify the notation, we denote the weak acid as HA and its anion as A^- . The reaction summary used here to analyze the extent of reaction was introduced in Section 11-1.

Problem-Solving Tip Selection of a van't Hoff Factor

Use an ideal value for the van't Hoff factor unless the question clearly indicates to do otherwise, as in the previous example and in some of the end-of-chapter exercises. For a strong electrolyte dissolved in water, the ideal value for its van't Hoff factor is listed in Table 14-3. For nonelectrolytes dissolved in water or any solute dissolved in common nonaqueous solvents, the van't Hoff factor is considered to be 1. For weak electrolytes dissolved in water, the van't Hoff factor is a little greater than 1.

14-15 Osmotic Pressure

Osmosis is the spontaneous process by which the solvent molecules pass through a semipermeable membrane from a solution of lower concentration of solute into a solution of higher concentration of solute. Figure 14-16a shows one type of experimental apparatus that demonstrates osmotic pressure. A **semipermeable membrane** such as cellophane separates the sugar solution from pure water. Solvent molecules (water in this case) may pass through the membrane in either direction, but the rate at which they pass into the more concentrated solution is initially greater than the rate in the opposite direction. The initial difference between the two rates is directly proportional to the difference in concentrations across the membrane. Solvent molecules continue to pass through the membrane until the hydrostatic pressure due to the increasing weight of the solution in the column forces the solvent molecules back through the membrane at the same rate at which they enter from the dilute side. The pressure exerted under this condition is called the **osmotic pressure** of the solution.

Osmotic pressure depends on the number, and not the kind, of solute particles in solution; it is therefore a colligative property.

The osmotic pressure of a given aqueous solution can be measured with an apparatus such as that depicted in Figure 14-16a. The solution of interest is placed inside an inverted glass (thistle) tube that has a semipermeable membrane firmly fastened across the bottom. This part of the thistle tube and its membrane are then immersed in a container of pure water. As time passes, the height of the solution in the neck rises until the back pressure it exerts counterbalances the osmotic pressure.

Alternatively, we can view osmotic pressure as the external pressure exactly sufficient to prevent osmosis. The pressure required (Figure 14-17) is equal to the osmotic pressure of the solution.

Like molecules of an ideal gas, solute particles are widely separated in very dilute solutions and do not interact significantly with one another. For very dilute solutions, osmotic pressure, π , is found to follow the equation

$$\pi = \frac{nRT}{V}$$

In this equation n is the number of moles of solute in volume, V (in liters), of the solution. The other quantities have the same meaning as in the ideal gas law. The term n/V is a concentration term. In terms of molarity, M ,

$$\pi = MRT$$

Osmotic pressure increases with increasing temperature because T affects the number of solvent-membrane collisions per unit time. It also increases with increasing molarity because M affects the difference in the numbers of solvent molecules hitting the membrane from the two sides, and because a higher M leads to a stronger drive to equalize the concentration difference by dilution and to increase disorder in the solution.

► Osmosis is one of the main ways in which water molecules move into and out of living cells. The membranes and cell walls in living organisms allow solvent to pass through. Some of these also selectively permit passage of ions and other small solute particles.

► The greater the concentration of solute particles, the greater the height to which the column rises, and the greater the osmotic pressure.

► For a solution of an electrolyte,

$$\pi = M_{\text{effective}}RT$$

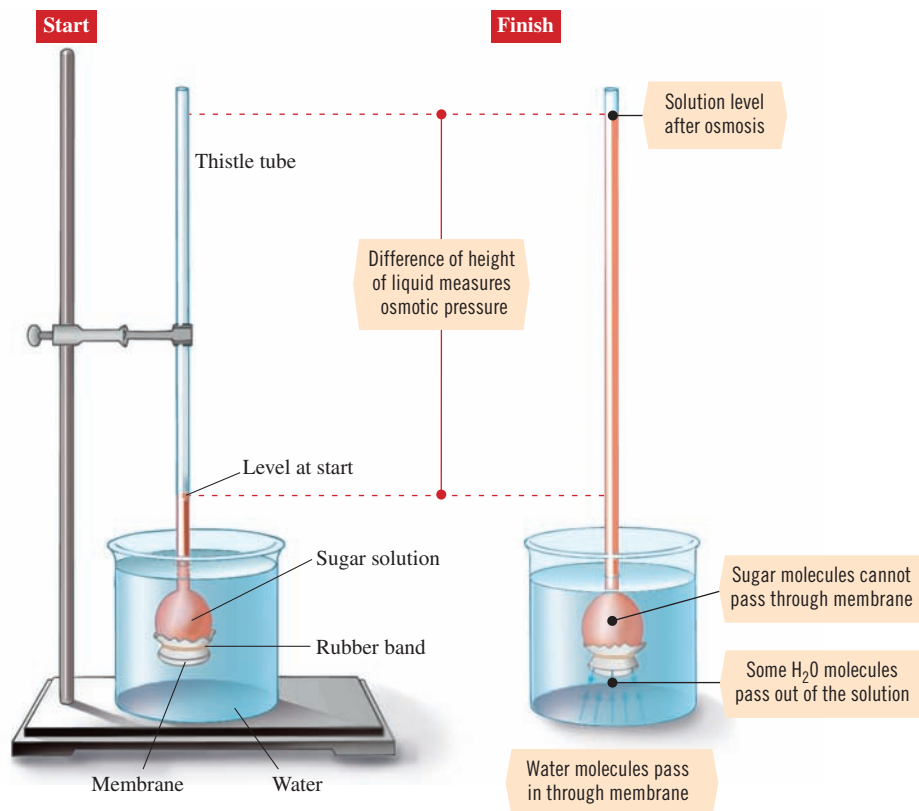
where $M_{\text{effective}} = iM_{\text{stated}}$

For *dilute aqueous solutions*, the molarity is approximately equal to the molality (because the density of the solution is nearly 1 g/mL or 1 kg/L), so

$$\pi = m_{\text{effective}}RT = im_{\text{stated}}RT$$

(dilute aqueous solutions)

Unless otherwise noted, all content on this page is © Cengage Learning.



A Laboratory apparatus for demonstrating osmosis. The picture at the right gives some details of the process.

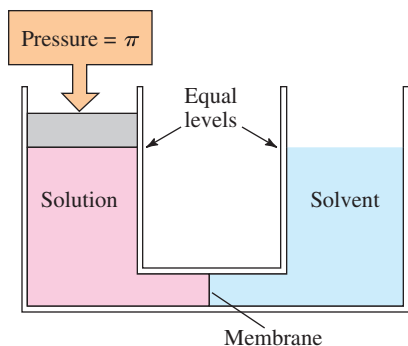
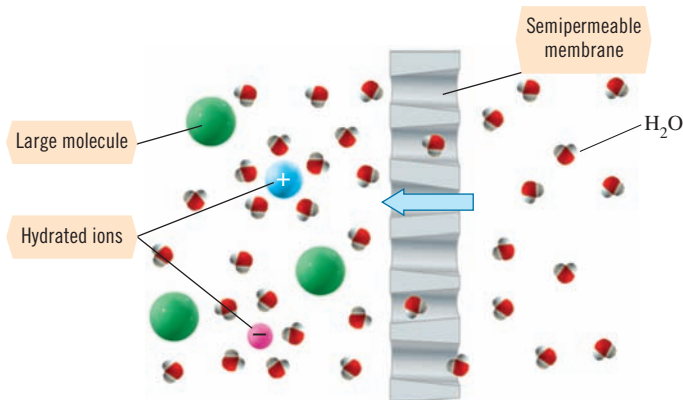


Figure 14-17 The pressure that is just sufficient to prevent solvent flow from the pure solvent side through the semipermeable membrane to the solution side is another measure of the osmotic pressure of the solution.



B A simplified representation of the function of a semipermeable membrane

Figure 14-16

EXAMPLE 14-13 Osmotic Pressure Calculation

What osmotic pressure would the 1.25 *m* sucrose solution in Example 14-2 exhibit at 25°C? The density of this solution is 1.34 g/mL.

Plan

We note that the approximation $M \approx m$ is not very good for this solution, because the density of this solution is quite different from 1 g/mL or kg/L. Thus, we must first find the molarity of sucrose, and then use the relationship $\pi = MRT$.

Solution

Recall from Example 14-2 that there is 50.0 g of sucrose (0.146 mol) in 117 g of H₂O, which gives 167 g of solution. Using the given density, we find that the volume of this solution is

$$\text{vol solution} = 167 \text{ g} \times \frac{1 \text{ mL}}{1.34 \text{ g}} = 125 \text{ mL or } 0.125 \text{ L}$$

Thus, the molarity of sucrose in the solution is

$$M_{\text{sucrose}} = \frac{0.146 \text{ mol}}{0.125 \text{ L}} = 1.17 \text{ mol/L}$$

Now we can calculate the osmotic pressure.

$$\pi = MRT = (1.17 \text{ mol/L}) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (298 \text{ K}) = 28.6 \text{ atm}$$

You should now work Exercise 84.

STOP & THINK

The osmotic pressure can be quite large and is usually expressed in atm units. The *R* value used here is the one that includes atm units.

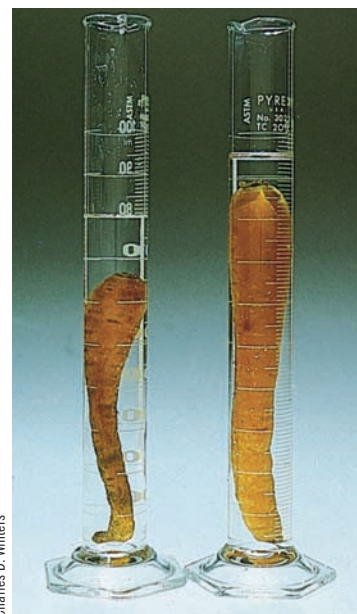
Let's compare the calculated values of the four colligative properties for the 1.25 *m* sucrose solution.

vapor pressure lowering	= 0.524 torr	(Example 14-4)
boiling point elevation	= 0.640°C	(Example 14-7)
freezing point depression	= 2.32°C	(Example 14-9)
osmotic pressure	= 28.6 atm	(Example 14-13)

The first of these is so small that it would be hard to measure precisely. Even this small lowering of the vapor pressure is sufficient to raise the boiling point by an amount that could be measured, although with difficulty. The freezing point depression is greater, but still could not be measured very precisely without a special apparatus. The osmotic pressure, on the other hand, is so large that it could be measured much more precisely. Thus, osmotic pressure is often the most easily measured of the four colligative properties, especially when very dilute solutions are used.

Osmotic pressures represent very significant forces. For example, a 1.00 molar solution of a nonelectrolyte in water at 0°C produces an equilibrium osmotic pressure of approximately 22.4 atmospheres (≈ 330 psi).

The use of measurements of osmotic pressure for the determination of molecular weights has several advantages. Even very dilute solutions give easily measurable osmotic pressures. This method is therefore useful in determination of the molecular weights of (1) very expensive substances, (2) substances that can be prepared only in very small amounts, and (3) substances of very high molecular weight that are not very soluble. Because high-molecular-weight materials are often difficult, and in some cases impossible, to obtain in a high state of purity, determinations of their molecular weights are not as accurate as we might like. Nonetheless, osmotic pressures provide a very useful method of estimating molecular weights.



Charles D. Winters

An illustration of osmosis. When a carrot is soaked in a concentrated salt solution, water flows out of the plant cells by osmosis. A carrot soaked overnight in salt solution (*left*) has lost much water and become limp. A carrot soaked overnight in pure water (*right*) is little affected.

EXAMPLE 14-14 Molecular Weight from Osmotic Pressure

Pepsin is an enzyme present in the human digestive tract. A solution of a 0.500-gram sample of purified pepsin in 30.0 mL of aqueous solution exhibits an osmotic pressure of 8.92 torr at 27.0°C. Estimate the molecular weight of pepsin.

► An enzyme is a protein that acts as a biological catalyst. Pepsin catalyzes the metabolic cleavage of amino acid chains (called peptide chains) in other proteins.

Unless otherwise noted, all content on this page is © Cengage Learning.

Plan

As we did in earlier molecular weight determinations (see Section 14-13), we must first find n , the number of moles that 0.500 grams of pepsin represents. We start with the equation $\pi = MRT$. The molarity of pepsin is equal to the number of moles of pepsin per liter of solution, n/V . We substitute this for M and solve for n .

Solution

$$\pi = MRT = \left(\frac{n}{V}\right) RT \quad \text{or} \quad n = \frac{\pi V}{RT}$$

We convert 8.92 torr to atmospheres to be consistent with the units of R .

$$n = \frac{\pi V}{RT} = \frac{\left(8.92 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}\right)(0.0300 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(300 \text{ K})} = 1.43 \times 10^{-5} \text{ mol pepsin}$$

Thus, 0.500 g of pepsin is 1.43×10^{-5} mol. We now estimate its molecular weight.

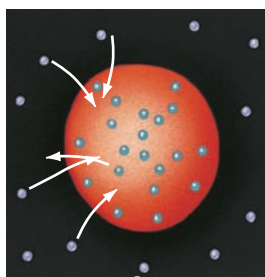
$$? \text{ g/mol} = \frac{0.500 \text{ g}}{1.43 \times 10^{-5} \text{ mol}} = 3.50 \times 10^4 \text{ g/mol}$$

The molecular weight of pepsin is approximately 35,000 amu. This is typical for medium-sized proteins.

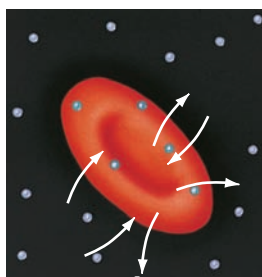
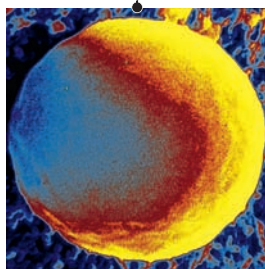
You should now work Exercise 90.

STOP & THINK

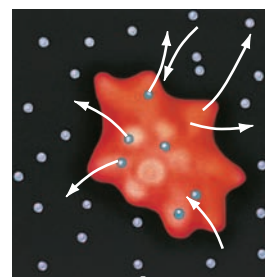
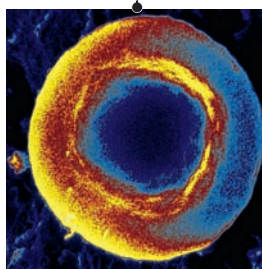
The freezing point depression of this very dilute solution would be only about 0.0009°C, which would be difficult to measure accurately. The osmotic pressure of 8.92 torr, on the other hand, is easily measured.



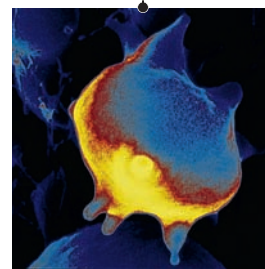
Cells expand in solution with lower electrolyte concentration (hypotonic). There is net flow of water *into* the cell until balanced by the osmotic pressure. This can lead to rupture and death of the cell.



Red blood cell in an isotonic solution. Blue spheres represent water molecules.



Cells shrink in a solution with greater electrolyte concentration (hypertonic). There is a net flow of water *out of* the cell until balanced by the osmotic pressure. This can lead to malfunctions and death of the cell.



DAVID PHILLIPS/SCIENCE SOURCE/PHOTO RESEARCHERS

Living cells contain solutions of salts (electrolytes). When a cell is put in contact with solutions having different electrolyte concentrations, the resulting osmotic pressure will cause a net flow of water to flow into (*left*) or out of (*right*) the cell causing it to expand or contract. The top row shows illustrations, while the bottom row shows actual scanning electron microscope images of red blood cells exhibiting these effects.

Problem-Solving Tip Units in Osmotic Pressure Calculations

The strict definition for osmotic pressure is in terms of molarity, $\pi = MRT$. Osmotic pressure, π , has the units of pressure (atmospheres); M (mol/L); and T (kelvins).

Therefore, the appropriate value of R is $0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$. We can balance the units in this equation as follows.

$$\text{atm} = \left(\frac{\text{mol}}{\text{L}} \right) \left(\frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (\text{K})$$

When we use the approximation that $M \approx m$, we might think that the units do not balance. For very dilute aqueous solutions, we can think of M as being *numerically* equal to m , but still having the units mol/L, as shown above.

Colloids

A solution is a homogeneous mixture in which no phase separation occurs and in which solutes are present as individual molecules or ions. This represents one extreme of mixtures. The other extreme is a suspension, a clearly heterogeneous mixture in which solute particles settle out after mixing with a solvent phase. Such a situation results when a handful of sand is stirred into water. **Colloids (colloidal dispersions)** represent an intermediate kind of mixture in which the solute particles, or **dispersed phase**, are suspended in the solvent phase, or **dispersing medium**. The particles of the dispersed phase are so small that settling is negligible. They are large enough, however, to scatter light as it passes through the colloid, making the mixture appear cloudy or even opaque.

Table 14-4 indicates that all combinations of solids, liquids, and gases can form colloids except mixtures of nonreacting gases (all of which are homogeneous and, therefore, true solutions). Whether a given mixture forms a solution, a colloidal dispersion, or a suspension depends on the size of the solute-like particles (Table 14-5), as well as solubility and miscibility.

14-16 The Tyndall Effect

Particles that are too small cannot scatter light. Solute particles in true solutions are below the size limit required for light scattering. Colloidal particles, however, are larger—up to about 10,000 Å (1000 nm or 1 micron)—so they do scatter light. This scattering of light by colloidal particles is called the **Tyndall effect** (Figure 14-18).

The scattering of light from automobile headlights by fogs and mists is an example of the Tyndall effect, as is the scattering of a light beam in a laser show by dust particles in the air in a darkened room. If the air didn't have any suspended solid particles you would not be able to see the laser beam.

14-17 The Adsorption Phenomenon

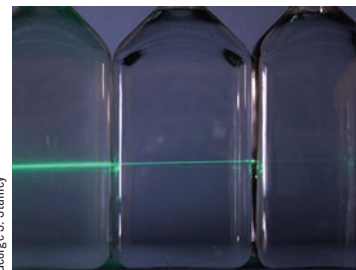
Much of the chemistry of everyday life is the chemistry of colloids, as one can tell from the examples in Table 14-4. Because colloidal particles are so finely divided, they have a tremendously high total surface area in relation to their volume. It is not surprising, therefore, that an understanding of colloidal behavior requires an understanding of surface phenomena.

Atoms on the surface of a colloidal particle are bonded only to other atoms of the particle on and below the surface. These atoms interact with whatever comes in contact



George Sample

Sports drinks were developed to counteract dehydration while maintaining electrolyte balance. Such solutions also help to prevent cell damage due to the osmotic pressure that would be caused by drinking large amounts of water.



George S. Stanley

Figure 14-18 The dispersion of a beam of light by colloidal particles is called the Tyndall effect. The rightmost container has distilled water that just barely scatters the green laser beam. The middle container is tap water that has small amounts of particles that do scatter the light to a moderate extent. The left container has 500 mL of distilled water with one drop of milk added. Milk is a colloid, so strong scattering of the laser beam is seen.

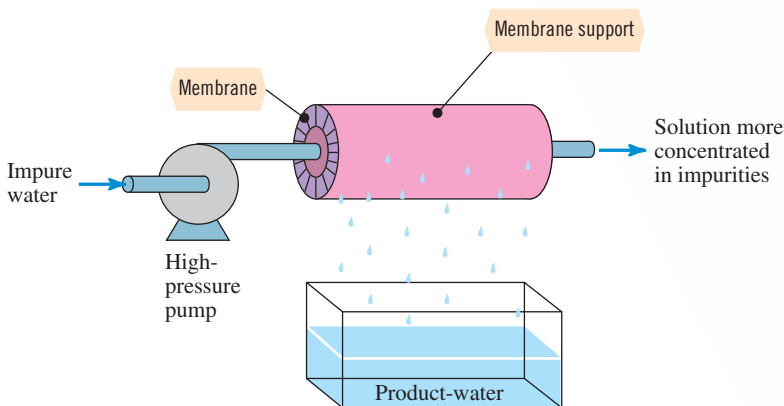
CHEMISTRY IN USE

Water Purification and Hemodialysis

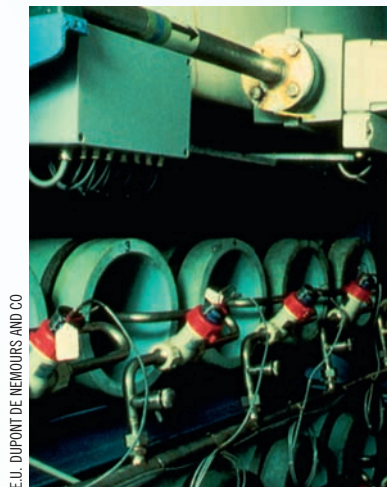
Semipermeable membranes play important roles in the normal functioning of many living systems. In addition, they are used in a wide variety of industrial and medical applications. Membranes with different permeability characteristics have been developed for many different purposes. One of these is the purification of water by reverse osmosis.

Suppose we place a semipermeable membrane between a saline (salt) solution and pure water. If the saline solution is pressurized under a greater pressure than its osmotic pressure, the direction of flow can be reversed. That is, the net flow of water molecules will be from the saline solution through the membrane into the pure water. This process is called **reverse osmosis**. The membrane usually consists of cellulose acetate or hollow fibers of a material structurally similar to nylon. This method has been used for the purification of brackish (mildly saline) water. It has the economic advantages of low cost, ease of apparatus construction, and simplicity of operation. Because this method of water purification requires no heat, it has a great advantage over distillation.

The city of Sarasota, Florida, has a large reverse osmosis plant to purify drinking water. It processes more than 4 million gallons of water per day from local wells. Total dissolved solids (mostly salts) are reduced in concentration from 1744 parts per million (ppm) (0.1744% by mass) to 90 ppm. This water is mixed with additional well water purified by an ion exchange system. The final product is more than 10 million gallons of water per day containing less than 500 ppm of total dissolved solids, the standard for drinking water set by the World Health



The reverse osmosis method of water purification.



A reverse osmosis unit used to provide all the fresh water (82,500 gallons per day) for the steamship *Norway*.

Organization. A large reverse osmosis plant in Ashkelon, Israel, processes seawater to produce more than 330,000 cubic meters per day (330 million L/day) of fresh water. This is enough to provide 13% of the country's domestic consumer demand. The Kuwaiti and Saudi water purification plants that were of strategic concern in the Persian Gulf War use reverse osmosis in one of their primary stages.

Human kidneys carry out many important functions. One of the most crucial is the removal of metabolic waste prod-



A portable reverse osmosis unit designed for individual use.

with the surface. Colloidal particles often adsorb ions or other charged particles, as well as gases and liquids. The process of **adsorption** involves adhesion of any such species onto the surfaces of particles. For example, a bright red **sol** (solid dispersed in liquid) is formed by mixing hot water with a concentrated aqueous solution of iron(III) chloride (Figure 14-19).



Freshly made wines are often cloudy because of colloidal particles. Removing these colloidal particles clarifies the wine.



The Tyndall effect is observed as the shafts of light created by the tree's foliage are scattered by the dust particles in the air.

Table 14-4 Types of Colloids

Dispersed (solute-like) Phase	Dispersing (solvent-like) Medium	Common Name	Examples
solid	in solid	solid sol	Many alloys (e.g., steel and duralumin), some colored gems, reinforced rubber, porcelain, pigmented plastics
liquid	in solid	solid emulsion	Cheese, butter, jellies
gas	in solid	solid foam	Sponge, rubber, pumice, Styrofoam
solid	in liquid	sols and gels	Milk of magnesia, paints, mud, puddings
liquid	in liquid	emulsion	Milk, face cream, salad dressings, mayonnaise
gas	in liquid	foam	Shaving cream, whipped cream, foam on beer
solid	in gas	solid aerosol	Smoke, airborne viruses and particulate matter, auto exhaust
liquid	in gas	liquid aerosol	Fog, mist, aerosol spray, clouds

Table 14-5 Approximate Sizes of Dispersed Particles

Mixture	Example	Approximate Particle Size
suspension	sand in water	larger than 10,000 Å
colloidal dispersion	starch in water	10–10,000 Å
solution	sugar in water	1–10 Å

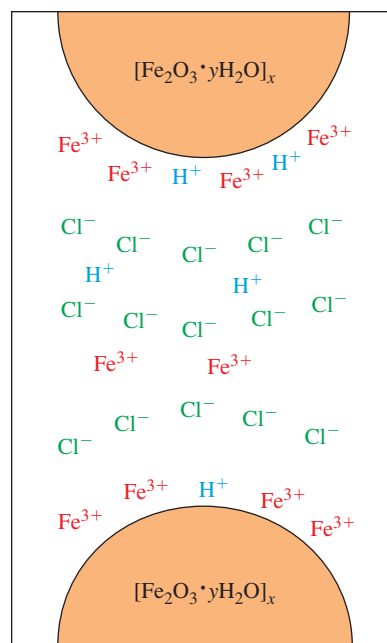


Figure 14-19 Stabilization of a colloid (Fe_2O_3 sol) by electrostatic forces. Each colloidal particle of this orange-red sol is a cluster of many formula units of hydrated Fe_2O_3 . Each cluster attracts positively charged Fe^{3+} ions to its surface. (Fe^{3+} ions fit readily into the crystal structure, so they, rather than the Cl^- ions, are preferentially adsorbed.) Each particle is then surrounded by a shell of positively charged ions, so the particles repel one another and cannot combine to the extent necessary to cause actual precipitation. The suspended particles scatter light, making the path of the light beam through the suspension visible.

14-18 Hydrophilic and Hydrophobic Colloids

Colloids are classified as **hydrophilic** (“water loving”) or **hydrophobic** (“water hating”) based on the surface characteristics of the dispersed particles.

Hydrophilic Colloids

Proteins such as the oxygen-carrier hemoglobin form hydrophilic sols when they are suspended in saline aqueous body fluids such as blood plasma. Such proteins are macromolecules (giant molecules) that fold and twist in an aqueous environment so that polar groups are exposed to the fluid, whereas nonpolar groups are encased (Figure 14-20). Protoplasm and human cells are examples of **gels**, which are special types of sols in which the solid particles (in this case mainly proteins and carbohydrates) join together in a semirigid network structure that encloses the dispersing medium. Other examples of gels are gelatin, jellies, and gelatinous precipitates such as $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$.

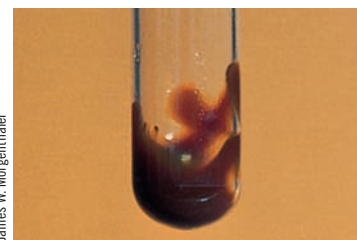
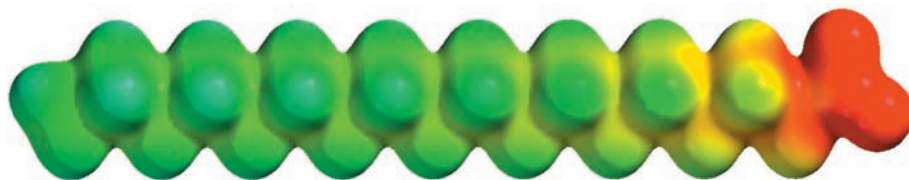
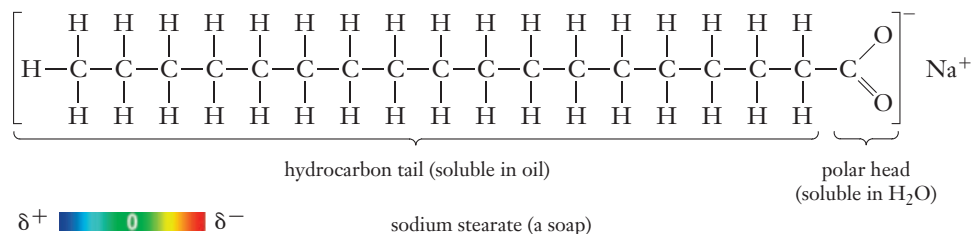
Hydrophobic Colloids

Hydrophobic colloids cannot exist in polar solvents without the presence of **emulsifying agents**, or **emulsifiers**. These agents coat the particles of the dispersed phase to prevent their coagulation into a separate phase. Milk and mayonnaise are examples of hydrophobic colloids (milk fat in milk, vegetable oil in mayonnaise) that stay suspended with the aid of emulsifying agents (casein in milk and egg yolk in mayonnaise).

Consider the mixture resulting from vigorous shaking of salad oil (nonpolar) and vinegar (polar). Droplets of hydrophobic oil are temporarily suspended in the water. In a short time, however, the very polar water molecules, which attract one another strongly, squeeze out the nonpolar oil molecules. The less dense oil then coalesces and floats to the top. If we add an emulsifying agent, such as egg yolk, and shake or beat the mixture, a stable emulsion (mayonnaise) results.

Oil and grease are mostly long-chain hydrocarbons that are very nearly nonpolar. Our most common solvent is water, a polar substance that does not dissolve nonpolar substances. To use water to wash soiled fabrics, greasy dishes, or our bodies, we must enable the water to suspend and remove nonpolar substances. Soaps and detergents are emulsifying agents that accomplish this. Their function is controlled by the intermolecular interactions that result from their structures.

Solid soaps are usually sodium salts of long-chain organic acids called fatty acids. They have a polar “head” and a nonpolar “hydrocarbon tail.” Sodium stearate, a typical soap, is shown here:



$\text{Fe}(\text{OH})_3$ is a gelatinous precipitate (a gel).

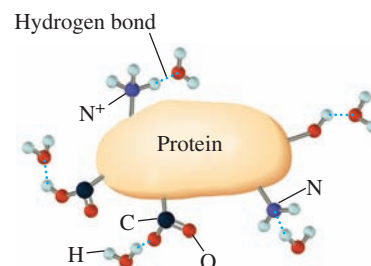


Figure 14-20 Examples of hydrophilic groups at the surface of a giant molecule (macromolecule) that help keep the macromolecule suspended in water.



Some edible colloids.

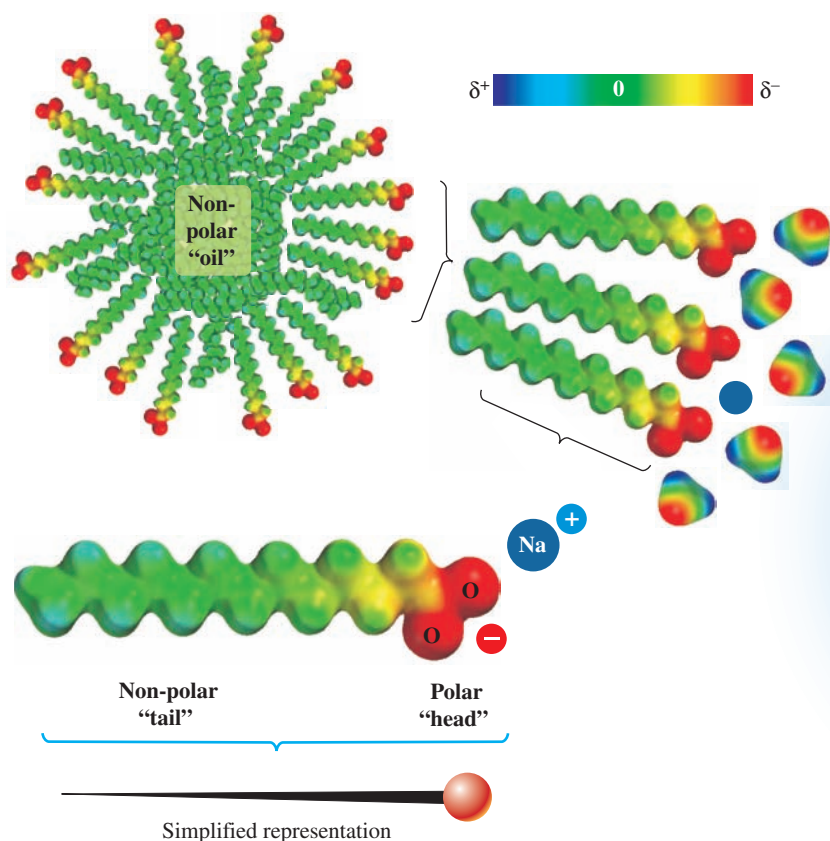
► “Dry” cleaning does not involve water. The organic solvents that are used in dry cleaning dissolve grease to form true solutions.



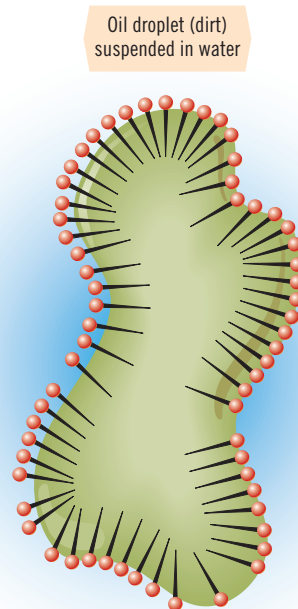
(Left) Powdered sulfur floats on pure water because of the high surface tension of water. (Right) When a drop of detergent solution is added to the water, its surface tension is lowered and sulfur sinks. This lowering of surface tension enhances the cleaning action of detergent solutions.

► Sodium stearate is also a major component of some stick deodorants.

The stearate ion is typical of the anions in soaps. It has a polar carboxylate head, —C(=O)O^- , and a long nonpolar tail, $\text{CH}_3(\text{CH}_2)_{16}\text{—}$. The head of the stearate ion is compatible with (“soluble in”) water, whereas the hydrocarbon tail is compatible with (“soluble in”) oil and grease. Groups of such ions can be dispersed in water because they form **micelles** (Figure 14-21a). Their “water-insoluble” nonpolar tails orient into the interior of a micelle, while their polar heads point to the outside where they can interact



A A representation of a micelle. The nonpolar tails “dissolve” in one another in the center of the cluster and the polar heads on the outside interact favorably with the polar water molecules.



B Attachment of soap or detergent molecules to a droplet of oily dirt to suspend it in water

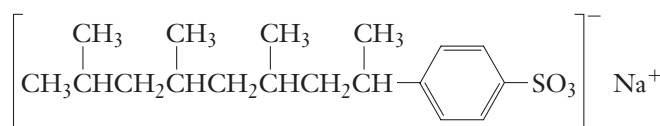
Figure 14-21 Two-dimensional representation of a micelle.

Unless otherwise noted, all content on this page is © Cengage Learning.

with the polar water molecules. When sodium stearate is stirred into water, the result is not a true solution. Instead it contains negatively charged micelles of stearate ions, surrounded by the positively charged Na^+ ions. The result is a suspension of micelles in water. These micelles are large enough to scatter light, so a soap–water mixture appears cloudy. Oil and grease “dissolve” in soapy water because the nonpolar oil and grease are preferentially absorbed into the nonpolar interior of micelles (see Figure 14-21b). Micelles form a true emulsion in water, so the oil and grease can be washed away. Sodium stearate is called a **surfactant** (meaning “surface-active agent”) or wetting agent because it has the ability to suspend and wash away oil and grease. Other soaps and detergents behave similarly.

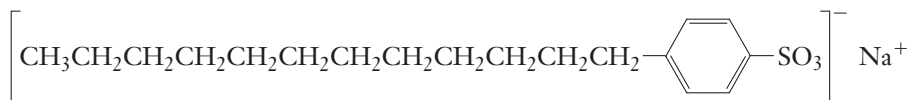
“**Hard**” water contains Fe^{3+} , Ca^{2+} , and/or Mg^{2+} ions, all of which displace Na^+ from soaps to form precipitates. This removes the soap from the water and puts an undesirable coating (“soap scum”) on the bathtub or on the fabric being laundered. Synthetic **detergents** are soap-like emulsifiers that contain sulfonate, $-\text{SO}_3^-$, or sulfate, $-\text{OSO}_3^-$, instead of carboxylate groups, $-\text{COO}^-$. They do not precipitate the ions of hard water due to their larger size and more delocalized negative charge (Coulomb’s Law, see Section 13-2) so they can be used in hard water as soap substitutes without forming undesirable scum.

Phosphates were added to commercial detergents for various purposes. They complexed the metal ions that contribute to water hardness and kept them dissolved, controlled acidity, and influenced micelle formation. The use of detergents containing phosphates is now discouraged because they cause **eutrophication** in rivers and streams that receive sewage. This is a condition (not related to colloids) in which an overgrowth of vegetation is caused by the high concentration of phosphorus, a plant nutrient. This overgrowth and the subsequent decay of the dead plants lead to decreased dissolved O_2 in the water, which causes the gradual elimination of marine life. There is also a foaming problem associated with branched alkylbenzenesulfonate (ABS) detergents in streams and in pipes, tanks, and pumps of sewage treatment plants. Such detergents are not **biodegradable**; that is, they cannot be broken down by bacteria.



a sodium branched alkylbenzenesulfonate (ABS)—a nonbiodegradable detergent

Currently used linear-chain alkylbenzenesulfonate (LAS) detergents are biodegradable and do not cause such foaming.



sodium lauryl benzenesulfonate

a linear alkylbenzenesulfonate (LAS)—a biodegradable detergent

Humic acids are a complex family of brown-colored natural components of plants (especially leaves and wood) that have multiple carboxylic acid groups and benzene rings. They are readily leached from decaying plant matter and often give streams a distinctive brownish color (Figure 14-22).



© Chinch Gryniewicz; Eosene/Corbis

Phosphates and nonbiodegradable detergents are responsible for the devastation of plant life in and along this river.

▶ The two detergents shown here each have a $\text{C}_{12}\text{H}_{25}$ tail, but the branched one is not biodegradable.



George Stanley

Figure 14-22 The Gooseberry River in northern Minnesota has a distinct brown color due to humic acids leached from decaying plant matter. These humic acids can act as natural detergents or surfactants, producing foams in the vicinity of rapids and waterfalls. The foaming in this case is not caused by synthetic detergents and is not a sign of pollution.

Unless otherwise noted, all content on this page is © Cengage Learning.

CHEMISTRY IN USE

Why Does Red Wine Go with Red Meat?

Choosing the appropriate wine to go with dinner is a problem for some diners. Experts, however, have offered a simple rule for generations, “serve red wine with red meat and white wine with fish and chicken.” Are these cuisine choices just traditions, or are there fundamental reasons for them?

Red wine is usually served with red meat because of a desirable matching of the chemicals found in each. The most influential ingredient in red meat is fat; it gives red meats their desirable flavor. As you chew a piece of red meat, the fat from the meat coats your tongue and palate, which desensitizes your taste buds. As a result, your second bite of red meat is less tasty than the first. Your steak would taste better if you washed your mouth between mouthfuls; there is an easy way to wash away the fat deposits.

Red wine contains a surfactant that cleanses your mouth, removing fat deposits, re-exposing your taste buds, and allowing you to savor the next bite of red meat almost as well as the first bite. The tannic acid (also called tannin) in red wine provides a soap-like action. Like soap, tannic acid consists of both a nonpolar complex hydrocarbon part as well as a polar one. The polar part of tannic acid dissolves in polar saliva, while the nonpolar part dissolves in the fat film that coats your palate. When you sip red wine, a suspension of micelles forms in the saliva. This micelle emulsion has the fat molecules in its interior; the fat is washed away by swallowing the red wine.

White wines go poorly with red meats because they lack the tannic acid needed to cleanse the palate. In fact, the presence



BRAND X PICTURES/GETTY IMAGES

or absence of tannic acid (not the color of the grapes) is what distinguishes red wines from white wines. Grapes fermented with their skins produce red wines; grapes fermented without their skins produce white wines.

Because fish and chicken have less fat than red meats, they can be enjoyed without surfactants to cleanse the palate. Also, the flavor of tannic acid can overpower the delicate flavor of many fish. The absence of tannic acid in white wines gives them a lighter flavor than red wines, and many people prefer this lighter flavor with their fish or chicken dinners.

RONALD DELORENZO

KEY TERMS

The following terms were defined at the end of Chapter 3: **concentration**, **dilution**, **molarity**, **percent by mass**, **solute**, **solution**, and **solvent**. The following terms were defined at the end of Chapter 13: **condensation**, **condensed phases**, **evaporation**, **phase diagram**, and **vapor pressure**.

Adsorption Adhesion of species onto surfaces of particles.

Associated ions Short-lived species formed by the collision of dissolved ions of opposite charge.

Biodegradability The ability of a substance to be broken down into simpler substances by bacteria.

Boiling point elevation The increase in the boiling point of a solvent caused by dissolution of a nonvolatile solute.

Boiling point elevation constant, K_b A constant that corresponds to the change (increase) in boiling point produced by a one-molal *ideal* solution of a nonvolatile nonelectrolyte.

Charge density of an ion The ionic charge divided by the ionic radius in angstroms.

Colligative properties Physical properties of solutions that depend on the number, but not the kind, of solute particles present.

Colloid A heterogeneous mixture in which solute-like particles do not settle out; also known as a *colloidal dispersion*.

Crystal lattice energy The energy change when one mole of formula units of a crystalline solid is formed from its ions, atoms, or molecules in the gas phase; always negative.

Detergent A soap-like emulsifier that contains a sulfonate, $-\text{SO}_3^-$, or sulfate, $-\text{OSO}_3^-$, group instead of a carboxylate, $-\text{COO}^-$, group.

Dispersed phase The solute-like species in a colloid.

Dispersing medium The solvent-like phase in a colloid.

Dispersion See *Colloid*.

Distillation The process in which components of a mixture are separated by boiling away the more volatile liquid.

Effective molality The sum of the molalities of all solute particles in solution.

Emulsifier See *Emulsifying agent*.

Emulsifying agent A substance that coats the particles of a dispersed phase and prevents coagulation of colloidal particles; an emulsifier; also known as an *emulsifier*.

Emulsion A colloidal dispersion of a liquid in a liquid.

Eutrophication The undesirable overgrowth of vegetation caused by high concentrations of plant nutrients in bodies of water.

Foam A colloidal dispersion of a gas in a liquid.

Fractional distillation The process in which a fractionating column is used in a distillation apparatus to separate components of a liquid mixture that have different boiling points.

Freezing point depression The decrease in the freezing point of a solvent caused by the presence of a solute.

Freezing point depression constant, K_f A constant that corresponds to the change in freezing point produced by a one-molal *ideal* solution of a nonvolatile nonelectrolyte.

Gel A colloidal dispersion of a solid in a liquid; a semirigid sol.

Hard water Water containing Fe^{3+} , Ca^{2+} , or Mg^{2+} ions, which form precipitates with soaps.

Heat of hydration See *Hydration energy (molar) of an ion*.

Heat of solution (molar) The amount of heat absorbed in the formation of a solution that contains one mole of solute; the value is positive if heat is absorbed (endothermic) and negative if heat is released (exothermic).

Henry's Law The concentration or solubility of a gas in a liquid at any given temperature is directly proportional to the partial pressure of the gas over the solution.

Hydration The interaction (surrounding) of solute particles with water molecules.

Hydration energy (molar) of an ion The energy change accompanying the hydration of a mole of gaseous ions.

Hydrophilic colloids Colloidal particles that attract water molecules.

Hydrophobic colloids Colloidal particles that repel water molecules.

Ideal solution A solution that obeys Raoult's Law exactly.

Liquid aerosol A colloidal dispersion of a liquid in a gas.

Micelle A cluster of a large number of soap or detergent molecules or ions, assembled with their hydrophobic tails directed toward the center and their hydrophilic heads directed outward.

Miscibility The ability of one liquid to mix with (dissolve in) another liquid.

Molality (m) Concentration expressed as number of moles of solute per kilogram of solvent.

Mole fraction of a component in solution The number of moles of the component divided by the total number of moles of all components.

Osmosis The process by which solvent molecules pass through a semipermeable membrane from a dilute solution into a more concentrated solution.

Osmotic pressure The hydrostatic pressure produced on the surface of a semipermeable membrane by osmosis.

Percent ionization of weak electrolytes The percent of the weak electrolyte that ionizes in a solution of a given concentration.

Raoult's Law The vapor pressure of a solvent in an ideal solution is directly proportional to the mole fraction of the solvent in the solution.

Reverse osmosis The forced flow of solvent molecules through a semipermeable membrane from a concentrated solution into a dilute solution. This is accomplished by application of hydrostatic pressure on the concentrated side greater than the osmotic pressure that is opposing it.

Saturated solution A solution in which no more solute will dissolve at a given temperature.

Semipermeable membrane A thin partition between two solutions through which certain molecules can pass but others cannot.

Soap An emulsifier that can disperse nonpolar substances in water; the sodium salt of a long-chain organic acid; consists of a long hydrocarbon chain attached to a carboxylate group, $-\text{CO}_2^- \text{Na}^+$.

Sol A colloidal dispersion of a solid in a liquid.

Solid aerosol A colloidal dispersion of a solid in a gas.

Solid emulsion A colloidal dispersion of a liquid in a solid.

Solid foam A colloidal dispersion of a gas in a solid.

Solid sol A colloidal dispersion of a solid in a solid.

Solvation The process by which solvent molecules surround and interact with solute ions or molecules.

Supersaturated solution A (metastable) solution that contains a higher-than-saturation concentration of solute; slight disturbance or seeding causes crystallization of excess solute.

Surfactant A "surface-active agent"; a substance that has the ability to emulsify and wash away oil and grease in an aqueous suspension.

Thermal pollution Introduction of heated waste water into natural waters.

Tyndall effect The scattering of light by colloidal particles.

van't Hoff factor (i) A number that indicates the extent of dissociation or ionization of a solute; equal to the actual colligative property divided by the colligative property calculated assuming no ionization or dissociation.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

General Concepts: The Dissolving Process

1. Support or criticize the statement "Solutions and mixtures are the same thing."

2. ● Give an example of a solution that contains each of the following: (a) a solid dissolved in a liquid; (b) a gas dissolved in a gas; (c) a gas dissolved in a liquid; (d) a liquid

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

- dissolved in a liquid; (e) a solid dissolved in a solid. Identify the solvent and the solute in each case.
- There are no *true* solutions in which the solvent is gaseous and the solute is either liquid or solid. Why?
 - Explain why (a) solute–solute, (b) solvent–solvent, and (c) solute–solvent interactions are important in determining the extent to which a solute dissolves in a solvent.
 - Define and distinguish between dissolution, solvation, and hydration.
 - The amount of heat released or absorbed in the dissolution process is important in determining whether the dissolution process is spontaneous, meaning, whether it can occur. What is the other important factor? How does it influence solubility?
 - An old saying is that “oil and water don’t mix.” Explain the molecular basis for this saying.
 - Two liquids, A and B, do not react chemically and are completely miscible. What would be observed as one is poured into the other? What would be observed in the case of two completely immiscible liquids and in the case of two partially miscible liquids?
 - Consider the following solutions. In each case, predict whether the solubility of the solute should be high or low. Justify your answers. (a) LiCl in *n*-octane, C₈H₁₈; (b) CaCl₂ in H₂O; (c) C₈H₁₈ in H₂O; (d) CHCl₃ in C₆H₁₄; (e) C₈H₁₈ in CCl₄
 - Consider the following solutions. In each case predict whether the solubility of the solute should be high or low. Justify your answers. (a) HCl in H₂O; (b) HF in H₂O; (c) Al₂O₃ in H₂O; (d) SiO₂ in H₂O; (e) Na₂(SO₄) in hexane, C₆H₁₄
 - For those solutions in Exercise 9 that can be prepared in “reasonable” concentrations, classify the solutes as nonelectrolytes, weak electrolytes, or strong electrolytes.
 - For those solutions in Exercise 10 that can be prepared in “reasonable” concentrations, classify the solutes as nonelectrolytes, weak electrolytes, or strong electrolytes.
 - Both methanol, CH₃OH, and ethanol, CH₃CH₂OH, are completely miscible with water at room temperature because of strong solvent–solute intermolecular attractions. Predict the trend in solubility in water for 1-propanol, CH₃CH₂CH₂OH; 1-butanol, CH₃CH₂CH₂CH₂OH; and 1-pentanol, CH₃CH₂CH₂CH₂CH₂OH.
 - (a) Does the solubility of a solid in a liquid exhibit an appreciable dependence on pressure? (b) Is the same true for the solubility of a liquid in a liquid? Why?
 - Describe a technique for determining whether or not a solution contains an electrolyte.
 - A reagent bottle in the storeroom is labeled as containing a sodium chloride solution. How can one determine whether or not the solution is saturated?
 - A handbook lists the value of the Henry’s Law constant as $3.31 \times 10^{-5} \text{ atm}^{-1}$ for ethane, C₂H₆, dissolved in water at 25°C. The absence of concentration units on *k* means that the constant is meant to be used with concentration expressed as a mole fraction. Calculate the mole fraction of ethane in water at an ethane pressure of 0.15 atm.
 - ▲ The mole fraction of methane, CH₄, dissolved in water can be calculated from the Henry’s Law constants of $2.42 \times 10^{-5} \text{ atm}^{-1}$ at 25°C and $1.73 \times 10^{-5} \text{ atm}^{-1}$ at 50°C. Calculate the solubility of methane at these temperatures for a methane pressure of 10. atm above the solution. Does the solubility increase or decrease with increasing temperature? (See Exercise 17 for interpretation of units.)
 - Choose the ionic compound from each pair for which the crystal lattice energy should be the most negative. Justify your choice. (a) LiF or LiBr; (b) KF or CaF₂; (c) FeF₂ or FeF₃; (d) NaF or KF
 - Choose the ion from each pair that should be more strongly hydrated in aqueous solution. Justify your choice. (a) Na⁺ or Rb⁺; (b) Cl[−] or Br[−]; (c) Fe³⁺ or Fe²⁺; (d) Na⁺ or Mg²⁺
 - ▲ The crystal lattice energy for LiBr(s) is −818.6 kJ/mol at 25°C. The hydration energy of the ions of LiBr(s) is −867.4 kJ/mol at 25°C (for infinite dilution). (a) What is the heat of solution of LiBr(s) at 25°C (for infinite dilution)? (b) The hydration energy of Li⁺(g) is −544 kJ/mol at 25°C. What is the hydration energy for Br[−](g) at 25°C?
 - Why is the dissolving of many ionic solids in water an endothermic process, whereas the mixing of most miscible liquids is an exothermic process?

Concentrations of Solutions

- Under what conditions are the molarity and molality of a solution nearly the same? Which concentration unit is more useful when measuring volume with burets, pipets, and volumetric flasks in the laboratory? Why?
- Many handbooks list solubilities in units of (g solute/100. g H₂O). How would you convert from this unit to mass percent?
- The density of a 15.00% by mass aqueous solution of acetic acid, CH₃COOH, is 1.0187 g/mL. What is (a) the molarity? (b) the molality? (c) the mole fraction of each component?
- Assume you dissolve 45.0 g of camphor, C₁₀H₁₆O, in 425 mL of ethanol, C₂H₅OH. Calculate the molality, mole fraction, and weight percent of camphor in this solution. (The density of ethanol is 0.785 g/mL.)
- ▲ Urea, (NH₂)₂CO, is a product of metabolism of proteins. An aqueous solution is 32.0% urea by mass and has a density of 1.087 g/mL. Calculate the molality of urea in the solution.
- Calculate the molality of a solution that contains 56.5 g of benzoic acid, C₆H₅COOH, in 350 mL of ethanol, C₂H₅OH. The density of ethanol is 0.789 g/mL.
- Sodium fluoride has a solubility of 3.84 g in 100.0 g of water at 18°C. Express this solute concentration in terms of (a) mass percent, (b) mole fraction, and (c) molality.
- What are the mole fractions of ethanol, C₂H₅OH, and water in a solution prepared by mixing 55.0 g of ethanol with 45.0 g of water?
- What are the mole fractions of ethanol, C₂H₅OH, and water in a solution prepared by mixing 55.0 mL of ethanol with 45.0 mL of water at 25°C? The density of ethanol is 0.789 g/mL, and that of water is 1.00 g/mL.

32. The density of an aqueous solution containing 12.50 g K_2SO_4 in 100.00 g solution is 1.083 g/mL. Calculate the concentration of this solution in terms of molarity, molality, percent of K_2SO_4 , and mole fraction of solvent.
33. ▲ A piece of jewelry is marked “14 carat gold,” meaning that on a mass basis the jewelry is 14/24 pure gold. What is the molality of gold in this alloy—considering the other metal as the solvent?
34. ▲ A solution that is 21.0% fructose, $\text{C}_6\text{H}_{12}\text{O}_6$, in water has a density of 1.10 g/mL at 20°C. (a) What is the molality of fructose in this solution? (b) At a higher temperature, the density is lower. Would the molality be less than, greater than, or the same as the molality at 20°C? Explain.
35. The density of a sulfuric acid solution taken from a car battery is 1.225 g/cm³. This corresponds to a 3.75 M solution. Express the concentration of this solution in terms of molality, mole fraction of H_2SO_4 , and percentage of water by mass.



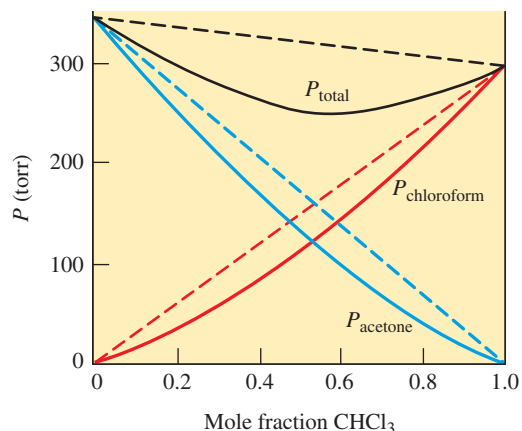
Charles D. Winters

Car battery

Raoult's Law and Vapor Pressure

36. ● In your own words, explain briefly *why* the vapor pressure of a solvent is lowered by dissolving a nonvolatile solute in it.
37. (a) Calculate the vapor pressure lowering associated with dissolving 20.2 g of table sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, in 400. g of water at 25.0°C. (b) What is the vapor pressure of the solution? Assume that the solution is ideal. The vapor pressure of pure water at 25.0°C is 23.76 torr. (c) What is the vapor pressure of the solution at 100.°C?
38. Calculate the vapor pressure of water over each of the following ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) solutions at 22°C (vp pure water = 19.83 torr). Ethylene glycol can be assumed to be nonvolatile.
- $X_{\text{ethylene glycol}} = 0.288$
 - % ethylene glycol by mass = 39.0%
 - 2.42 m ethylene glycol
39. At -100.°C ethane, CH_3CH_3 , and propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, are liquids. At this temperature, the vapor pressure of pure ethane is 394 torr and that of pure propane is 22 torr. What is the vapor pressure at -100.°C over a solution containing equal molar amounts of these substances?
40. Using Raoult's Law, predict the partial pressures in the vapor above a solution containing 0.550 mol acetone ($P^0 = 345$ torr) and 0.550 mol chloroform ($P^0 = 295$ torr).
41. What is the composition of the vapor above the solution described in Exercise 39?
42. What is the composition of the vapor above the solution described in Exercise 40?

43. Use the following vapor pressure diagram to estimate (a) the partial pressure of chloroform, (b) the partial pressure of acetone, and (c) the total vapor pressure of a solution in which the mole fraction of CHCl_3 is 0.30, assuming *ideal* behavior.



44. Answer Exercise 43 for the *real* solution of acetone and chloroform.
45. A solution is prepared by mixing 50.0 g of dichloromethane, CH_2Cl_2 , and 30.0 g of dibromomethane, CH_2Br_2 , at 0°C. The vapor pressure at 0°C of pure CH_2Cl_2 is 0.175 atm, and that of CH_2Br_2 is 0.0150 atm. (a) Assuming ideal behavior, calculate the total vapor pressure of the solution. (b) Calculate the mole fractions of CH_2Cl_2 and CH_2Br_2 in the *vapor* above the liquid. Assume that both the vapor and the solution behave ideally.

Boiling Point Elevation and Freezing Point Depression: Solutions of Nonelectrolytes

46. Calculate the boiling point of a 2.97 m aqueous solution of ethylene glycol, a nonvolatile nonelectrolyte.



Charles Steele

Ethylene glycol solutions

47. A solution is prepared by dissolving 8.89 g of ordinary sugar (sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, 342 g/mol) in 34.0 g of water. Calculate the boiling point of the solution. Sucrose is a nonvolatile nonelectrolyte.
48. What is the freezing point of the solution described in Exercise 46?



Molecular Reasoning exercises



More Challenging exercises

Blue-Numbered

exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

49. What is the freezing point of the solution described in Exercise 47?
50. Refer to Table 14-2. Suppose you had a 0.175 *m* solution of a nonvolatile nonelectrolyte in each of the solvents listed there. Which one should have (a) the greatest freezing point depression, (b) the lowest freezing point, (c) the greatest boiling point elevation, and (d) the highest boiling point?
51. A 5.00% solution of dextrose, $C_6H_{12}O_6$, in water is referred to as DW₅. This solution can be used as a source of nourishment when introduced by intravenous injection. Calculate the freezing point and the boiling point of a DW₅ solution.
52. Lemon juice is a complex solution that does not freeze in a home freezer at temperatures as low as -11°C . At what temperature will the lemon juice freeze if its effective molality is the equivalent of a 10.0 *m* glucose solution?
53. ▲ The “proof” of an alcoholic beverage is twice the volume percent of ethanol, C_2H_5OH , in water. The density of ethanol is 0.789 g/mL and that of water is 1.00 g/mL. A bottle of 100-proof rum is left outside on a cold winter day. (a) Will the rum freeze if the temperature drops to -18°C ? (b) Rum is used in cooking and baking. At what temperature does 100-proof rum boil?
54. A 3.0-g sample of a nonelectrolyte was isolated from beef fat. The molecular weight of the compound was determined to be 137 amu. The sample was dissolved in 250.0 mL of ethanol. At what temperature should the solution boil? For ethanol: boiling point = 78.41°C , $K_b = 1.22^\circ\text{C}/m$, density = 0.789 g/mL.
55. The normal boiling point of benzene is 80.1°C . A 0.85-gram sample of a nonvolatile compound with the molar mass of 185 g/mol is dissolved in 2.75 g of benzene. What is the expected boiling point of this solution?
56. Pure copper melts at 1083°C . Its molal freezing point depression constant is $23^\circ\text{C}/m$. What will be the melting point of a brass made of 12% Zn and 88% Cu by mass?
57. How many grams of the nonelectrolyte sucrose, $C_{12}H_{22}O_{11}$, should be dissolved in 725 g of water to produce a solution that freezes at -1.85°C ?
58. An aqueous solution contains 0.180 g of an unknown, nonionic solute in 50.0 g of water. The solution freezes at -0.040°C . What is the molar mass of the solute?
59. A solution was made by dissolving 3.75 g of a nonvolatile solute in 108.7 g of acetone. The solution boiled at 56.58°C . The boiling point of pure acetone is 55.95°C , and $K_b = 1.71^\circ\text{C}/m$. Calculate the molecular weight of the solute.
60. The molecular weight of an organic compound was determined by measuring the freezing point depression of a benzene solution. A 0.500-g sample was dissolved in 75.0 g of benzene, and the resulting depression was 0.53°C . What is the approximate molecular weight? The compound gave the following elemental analysis: 37.5% C, 12.5% H, and 50.0% O by mass. Determine the formula and exact molecular weight of the substance.
61. When 0.154 g of sulfur is finely ground and melted with 4.38 g of camphor, the freezing point of the camphor is lowered by 5.47°C . What is the molecular weight of sulfur? What is its molecular formula?
62. ▲ (a) Suppose we dissolve a 6.00-g sample of a mixture of naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$, in 360. g

of benzene. The solution is observed to freeze at 4.85°C . Find the percent composition (by mass) of the sample.
 (b) At what temperature should the solution boil? Assume that naphthalene and anthracene are nonvolatile nonelectrolytes.

Boiling Point Elevation and Freezing Point Depression: Solutions of Electrolytes

63. ● Explain ion association in solution. Can you suggest why the term “ion pairing” is sometimes used to describe this phenomenon?
64. ● You have separate 0.10 *M* aqueous solutions of the following salts: LiNO_3 , $\text{Ca}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$. In which one would you expect to find the highest particle concentration? Which solution would you expect to conduct electricity most strongly? Explain your reasoning.
65. ● What is the significance of the van't Hoff factor, *i*?
66. ● What is the value of the van't Hoff factor, *i*, for the following strong electrolytes at infinite dilution? (a) Na_2SO_4 ; (b) NaOH ; (c) $\text{Al}_2(\text{SO}_4)_3$; (d) CaSO_4 .
67. ● Compare the number of solute particles that are present in equal volumes of solutions of equal concentrations of strong electrolytes, weak electrolytes, and nonelectrolytes.
68. ● Four beakers contain 0.010 *m* aqueous solutions of CH_3OH , KClO_3 , CaCl_2 , and CH_3COOH , respectively. Without calculating the actual freezing points of each of these solutions, arrange them from lowest to highest freezing point.
69. ▲ A 0.050 *m* aqueous solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ has a freezing point of -0.2800°C . Calculate the total concentration of solute particles in this solution, and interpret your results.
70. ▲ A solution is made by dissolving 1.25 grams each of NaCl , NaBr , and NaI in 150. g of water. What is the vapor pressure above this solution at 100°C ? Assume complete dissociation of the three salts.
71. The ice fish lives under the polar ice cap where the water temperature is -4°C . This fish does not freeze at that temperature due to the solutes in its blood. The solute concentration of the fish's blood can be related to a sodium chloride solution that would have the same freezing point. What is the minimum concentration of a sodium chloride solution that would not freeze at -4°C ? Assume ideal behavior and complete dissociation of NaCl .
72. ● Which solution would freeze at a lower temperature, 0.100 *m* sodium sulfate or 0.100 *m* calcium sulfate? Explain without calculation.
73. ● Two solutions are produced by dissolving 10.0 grams of sodium nitrate in 0.500 kg of water and by dissolving 10.0 grams of calcium nitrate in 0.500 kg of water. Which solution would freeze at a lower temperature? Explain without calculation.
74. ● A series of 1.1 *m* aqueous solutions is produced. Predict without calculation which solution in each pair would boil at the higher temperature. (a) NaCl or LiCl ; (b) NaCl or Na_2SO_4 ; (c) Na_2SO_4 or HCl ; (d) HCl or $\text{C}_6\text{H}_{12}\text{O}_6$; (e) $\text{C}_6\text{H}_{12}\text{O}_6$ or CH_3OH ; (f) CH_3OH or CH_3COOH ; (g) CH_3COOH or KCl .
75. ● Identify without calculation which of the following solutions, each prepared by dissolving 65.0 g of the solute

- in 150. mL of water, would display the highest boiling point, and explain your choice. (a) NaCl or LiCl; (b) LiCl or Li_2SO_4 ; (c) Na_2SO_4 or HCl; (d) HCl or $\text{C}_6\text{H}_{12}\text{O}_6$; (e) $\text{C}_6\text{H}_{12}\text{O}_6$ or CH_3OH ; (f) CH_3OH or CH_3COOH ; (g) CH_3COOH or KCl.
76. What is the boiling point of a solution composed of 15.0 g urea, $(\text{NH}_2)_2\text{CO}$, in 0.500 kg water?
77. Estimate the freezing point of an aqueous solution that contains 2.0 moles of CaCl_2 in 1000. grams of water.
78. A 0.100 *m* acetic acid solution in water freezes at -0.188°C . Calculate the percent ionization of CH_3COOH in this solution.
79. ▲ In a home ice cream freezer, we lower the freezing point of the water bath surrounding the ice cream container by dissolving NaCl in water to make a brine solution. A 15.0% brine solution is observed to freeze at -10.89°C . What is the van't Hoff factor, *i*, for this solution?



Ice cream

80. CsCl dissolves in water according to



A 0.121 *m* solution of CsCl freezes at -0.403°C . Calculate *i* and the apparent percent dissociation of CsCl in this solution.

Osmotic Pressure

81. ● What are osmosis and osmotic pressure?
82. ▲ Show numerically that the molality and molarity of 1.00×10^{-4} *M* aqueous sodium chloride are nearly equal. Why is this true? Would this be true if another solvent, say acetonitrile, CH_3CN , replaced water? Why or why not? The density of CH_3CN is 0.786 g/mL at 20.0°C .
83. Show how the expression $\pi = MRT$, where π is osmotic pressure, is similar to the ideal gas law. Rationalize qualitatively why this should be so.
84. What is the osmotic pressure associated with a 0.0200 *M* aqueous solution of a nonvolatile nonelectrolyte solute at 75°C ?
85. The osmotic pressure of an aqueous solution of a nonvolatile nonelectrolyte solute is 1.21 atm at 0.0°C . What is the molarity of the solution?
86. Calculate the freezing point depression and boiling point elevation associated with the solution in Exercise 85.
87. Estimate the osmotic pressure associated with 12.5 g of an enzyme of molecular weight 4.21×10^6 dissolved in 1500. mL of ethyl acetate solution at 38.0°C .
88. Calculate the osmotic pressure at 25°C of 1.20 *m* K_2CrO_4 in water, taking ion association into account. Refer to Table 14-3. The density of a 1.20 *m* K_2CrO_4 solution is 1.25 g/mL.
89. Estimate the osmotic pressure at 25°C of 1.20 *m* K_2CrO_4 in water, assuming no ion association. The density of a 1.20 *m* K_2CrO_4 solution is 1.25 g/mL.
90. ▲ Many biological compounds are isolated and purified in very small amounts. We dissolve 11.0 mg of a biological macromolecule with a molecular weight of 2.00×10^4 in 10.0 g of water. (a) Calculate the freezing point of the solution. (b) Calculate the osmotic pressure of the solution at 25°C . (c) Suppose we are trying to use freezing point measurements to determine the molecular weight of this substance and that we make an error of only 0.001°C in the temperature measurement. What percent error would this cause in the calculated molecular weight? (d) Suppose we could measure the osmotic pressure with an error of only 0.1 torr (not a very difficult experiment). What percent error would this cause in the calculated molecular weight?

Colloids

91. ● How does a colloidal dispersion differ from a true solution?
92. Distinguish among (a) sol, (b) gel, (c) emulsion, (d) foam, (e) solid sol, (f) solid emulsion, (g) solid foam, (h) solid aerosol, and (i) liquid aerosol. Try to give an example of each that is not listed in Table 14-4.
93. ● What is the Tyndall effect, and how is it caused?
94. ● Distinguish between hydrophilic and hydrophobic colloids.
95. ● What is an emulsifier?
96. ● Distinguish between soaps and detergents. How do they interact with hard water? Write an equation to show the interaction between a soap and hard water that contains Ca^{2+} ions.
97. What is the disadvantage of branched alkylbenzenesulfonate (ABS) detergents compared with linear alkylbenzenesulfonate (LAS) detergents?

Mixed Exercises

98. ▲ An aqueous solution prepared by dissolving 1.56 g of anhydrous AlCl_3 in 50.0 g of water has a freezing point of -1.61°C . Calculate the boiling point and osmotic pressure at 25°C of this solution. The density of the solution at 25°C is 1.002 g/mL. K_f and K_b for water are $1.86^\circ\text{C}/m$ and $0.512^\circ\text{C}/m$, respectively.
99. Dry air contains 20.94% O_2 by volume. The solubility of O_2 in water at 25°C is 0.041 gram O_2 per liter of water. How many liters of water would dissolve the O_2 in one liter of dry air at 25°C and 1.00 atm?
100. (a) The freezing point of a 1.00% aqueous solution of acetic acid, CH_3COOH , is -0.310°C . What is the approximate formula weight of acetic acid in water? (b) A 1.00% solution of acetic acid in benzene has a



Molecular Reasoning exercises



More Challenging exercises

Blue-Numbered

exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

- freezing point depression of 0.441°C . What is the formula weight of acetic acid in this solvent? Explain the difference.
101. An aqueous ammonium chloride solution contains 5.75 mass % NH_4Cl . The density of the solution is 1.0195 g/mL . Express the concentration of this solution in molarity, molality, and mole fraction of solute.
 102. ● Starch contains $\text{C}-\text{C}$, $\text{C}-\text{H}$, $\text{C}-\text{O}$, and $\text{O}-\text{H}$ bonds. Hydrocarbons contain only $\text{C}-\text{C}$ and $\text{C}-\text{H}$ bonds. Both starch and hydrocarbon oils can form colloidal dispersions in water. (a) Which dispersion is classified as hydrophobic? (b) Which is hydrophilic? (c) Which dispersion would be easier to make and maintain?
 103. ▲ Suppose we put some one-celled microorganisms in various aqueous NaCl solutions. We observe that the cells remain unperturbed in 0.7% NaCl , whereas they shrink in more concentrated solutions and expand in more dilute solutions. Assume that 0.7% NaCl behaves as an *ideal* 1:1 electrolyte. Calculate the osmotic pressure of the aqueous fluid within the cells at 25°C .
 104. ▲ A sample of a drug ($\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}$, molecular weight = 369 g/mol) mixed with lactose (a sugar, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, molecular weight = 342 g/mol) was analyzed by osmotic pressure to determine the amount of sugar present. If 100. mL of solution containing 1.00 g of the drug–sugar mixture has an osmotic pressure of 519 torr at 25°C , what is the percent sugar present?
 105. A solution containing 4.52 g of a nonelectrolyte polymer per liter of benzene solution has an osmotic pressure of 0.786 torr at 20.0°C . (a) Calculate the molecular weight of the polymer. (b) Assume that the density of the dilute solution is the same as that of benzene, 0.879 g/mL . What would be the freezing point depression for this solution? (c) Why are boiling point elevations and freezing point depressions difficult to use to measure molecular weights of polymers?
 106. ● On what basis would you choose the components to prepare an ideal solution of a molecular solute? Which of the following combinations would you expect to act most nearly ideally? (a) $\text{CH}_4(\ell)$ and $\text{CH}_3\text{OH}(\ell)$; (b) $\text{CH}_3\text{OH}(\ell)$ and $\text{NaCl}(\text{s})$; (c) $\text{CH}_4(\ell)$ and $\text{CH}_3\text{CH}_3(\ell)$.
 107. Physiological saline (normal saline) is a 0.90% NaCl solution. This solution is isotonic with human blood. Calculate the freezing point and boiling point of physiological saline. Assume complete dissociation.
 108. A mixture used in parasitology “for clearing large nematodes” consists of 500 mL of glycerol, 300 mL of 95% ethanol (by volume), and 200 mL of water. Calculate the volume of pure ethanol, the total volume of water, the mass of each component, the number of moles of each component, and the mole fraction of each component. (densities: glycerol = 1.26 g/mL , ethanol = 0.789 g/mL , and water = 0.998 g/mL) If you were to pick one component as the solvent, would it be by volume, mass, or number of moles?
- unchanged: (a) decreasing the ionic charge (such as from Cu^{2+} to Cu^{+}); (b) increasing the ionic radius (such as from $1.66\text{ \AA}$ for Rb^{+} to $1.81\text{ \AA}$ for Cs^{+})?
110. Many gases are only minimally soluble in water because they are not capable of hydrogen bonding with water, they do not ionize extensively, and they do not react with water. Explain the relatively high solubility of each of the following gases in water: H_2S (3.5 g/L), SO_2 (106.4 g/L), and NH_3 (520 g/L).
 111. Unlike molarity, the molality of a solution is independent of the temperature of the solution. Examine the defining formulas for molarity and molality. Why does the molarity of a solution change with a change in temperature while the molality does not?
 112. What effects does adding a solute to a solvent, thereby producing a solution, have on the following properties of the solution, compared with those of the pure solvent? It (a) _____ the vapor pressure, (b) _____ the boiling point, (c) _____ the freezing point, and (d) _____ the osmotic pressure.
 113. Ideally, how many particles (molecules or ions) are produced per formula unit when each of the following substances is dissolved in water: ethylene glycol [$\text{C}_2\text{H}_4(\text{OH})_2$], a nonelectrolyte, barium hydroxide [$\text{Ba}(\text{OH})_2$], potassium phosphate (K_3PO_4), and ammonium nitrate (NH_4NO_3)?
 114. In the first five sections of this chapter, the term “dissolution” was used to describe the process by which a solute is dispersed by a solvent to form a solution. A popular dictionary defines dissolution as “decomposition into fragments or parts.” Using either of the definitions, compare the following two uses of the term. “It was ruled that there must be dissolution of the estate.” “The ease of dissolution of a solute depends on two factors.”
 115. ▲ Consider two nonelectrolytes A and B; A has a higher molecular weight than B, and both are soluble in solvent C. A solution is made by dissolving x grams of A in 100 grams of C; another solution is made by dissolving the same number of grams, x , of B in 100 grams of C. Assume that the two solutions have the same density. (a) Which solution has the higher molality? (b) Which solution has the higher mole fraction? (c) Which solution has the higher percent by mass? (d) Which solution has the higher molarity?
 116. ● The actual value for the van’t Hoff factor, i , is often observed to be less than the ideal value. Less commonly, it is greater than the ideal value. Give molecular explanations for cases where i is observed to be greater than the ideal value.
 117. ▲ A 1.0 m aqueous solution of a monoprotic acid freezes at -3.35°C , 2.0 m solution of the acid freezes at -6.10°C , and 4.0 m solution of a monoprotic acid freezes at -8.70°C . Calculate the van’t Hoff factor, i , for the acid at each concentration. Plot i versus concentration, and from the graph determine the value of i for the 3.0 m solution. Describe the general trend of the value of i versus concentration.
 118. Using the data in Exercise 117, calculate the percent ionization for the acid in 1.0 m , 2.0 m , and 4.0 m solutions. Describe the general trend of the value of percent ionization versus concentration.
 119. ▲ When the van’t Hoff factor, i , is included, the boiling point elevation equation becomes $\Delta T_b = iK_b m$. The van’t Hoff factor can be inserted in a similar fashion in the

Conceptual Exercises

109. Hydration energies for ions generally increase (become more negative) as their charge/radius ratio increases. What effect would you expect each of the following changes to have on the hydration energies if all other factors are

freezing point depression equation and the osmotic pressure equation. The van't Hoff factor, however, cannot be inserted in the same way into the vapor pressure-lowering equation. Show algebraically that $\Delta P_{\text{solvent}} = iX_{\text{solute}}P_{\text{solvent}}^0$ is not equivalent to $\Delta P_{\text{solvent}} = \{(ix \text{ moles}_{\text{solute}})/[(ix \text{ moles}_{\text{solute}}) + (\text{moles}_{\text{solvent}})]\}P_{\text{solvent}}^0$. Which equation for $\Delta P_{\text{solvent}}$ is correct?

120. The two solutions shown were both prepared by dissolving 194 g of K_2CrO_4 (1.00 mol) in a 1.00-L volumetric flask. The solution on the right was diluted to the 1-L mark on the neck of the flask, and the solution on the left was diluted by adding 1.00 L of water. Which solution, the one on the left or the one on the right, is (a) more concentrated; (b) a 1.00 *m* solution; (c) a 1.00 *M* solution?



Charles D. Winters

Chromate solutions

121. Would you expect lowering the freezing point or elevating the boiling point to be the better method to obtain the approximate molecular weight of an unknown? Explain your choice.
122. Rock candy consists of crystals of sugar on a string or stick. Propose a method of making rock candy, and explain each step.
123. Concentrations expressed in units of parts per million and parts per billion often have no meaning for people until they relate these small and large numbers to their own experiences. How many seconds are equal to 1 ppm of a year?

Building Your Knowledge

124. DDT is a toxin still found in the fatty tissues of some animals. DDT was transported into our lakes and streams as runoff from agricultural operations where it was originally used several years ago as an insecticide. In the lakes and streams it did not dissolve to any great extent; it collected in the lake and stream bottoms. It entered the bodies of animals via fatty tissues in their diet; microorganisms collected the DDT, the fish ate the microorganisms, and so on. Fortunately, much of the once large quantities of DDT in lakes and streams has biodegraded. Based on this information, what can you conclude regarding the intermolecular forces present in DDT?
125. Draw Figure 14-1, but instead of using colored circles to represent the solvent and solute molecules, draw

ball-and-stick models to represent water as the solvent and acetone, CH_3COCH_3 , as the solute. Use dashed lines to show hydrogen bonds. Twelve water molecules and two acetone molecules should be sufficient to illustrate the interaction between these two kinds of molecules.

126. A sugar maple tree grows to a height of about 40 feet, and its roots are in contact with water in the soil. What must be the concentration of the sugar in its sap if osmotic pressure is solely responsible for forcing the sap to the top of the tree at 15°C? The density of mercury is 13.6 g/cm³, and the density of the sap can be considered to be 1.10 g/cm³.
127. Many metal ions become hydrated in solution by forming coordinate covalent bonds with the unshared pair of electrons from the water molecules to form “ AB_6 ” ions. Because of their sizes, these hydrated ions are unable to pass through the semipermeable membrane described in Section 14-15, whereas water as a trimer, $(\text{H}_2\text{O})_3$, or a tetramer, $(\text{H}_2\text{O})_4$, can pass through. Anions tend to be less hydrated. Using the VSEPR theory, prepare three-dimensional drawings of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ and a possible $(\text{H}_2\text{O})_3$ that show their relative shapes and sizes.

Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

128. Use an internet search engine (such as <http://www.google.com>) to find the circumference of Earth at its equator. What is 1.00 ppm of this length?
129. Use an internet search engine (such as <http://www.google.com>) to locate information on the first winner of the Nobel Prize in Chemistry. With what colligative property do we associate his name?
130. Use an internet search engine (such as <http://www.google.com>) to locate information on the scientist John Tyndall. (a) What colloidal property has John Tyndall's name associated with it? (b) John Tyndall died due to a drug overdose that had been secretly administered by his wife in an effort to treat an ailment that had plagued him for several years. What ailment was his wife attempting to treat?
131. Use an internet search engine (such as <http://www.google.com>) to locate information on edible colloids. (a) Give the addresses of three sites that discuss edible colloids. (b) List eight edible colloids that are not also listed in Table 14-4. (c) Is ice cream an emulsion, a foam, or a sol? (d) Is any part of Spam a colloid?
132. Use an internet search engine (such as <http://www.google.com>) to locate information on thixotropy. Describe the relationship between thixotropy and the molecular properties of some colloids.
133. Use an internet search engine (such as <http://www.google.com>) to locate information on fractional distillation of petroleum. List the names and boiling point ranges of six or more distillation fractions usually obtained from most crude petroleum.



Chemical Thermodynamics

15



Thousands of windmills such as these in west Texas are becoming an increasingly important source of electricity. The kinetic energy of wind turns large windmill-powered turbines, which in turn convert their kinetic energy to electrical (potential) energy.

Raymond E. Davis

OUTLINE

Heat Changes and Thermochemistry

- 15-1** The First Law of Thermodynamics
- 15-2** Some Thermodynamic Terms
- 15-3** Enthalpy Changes
- 15-4** Calorimetry: Measurement of Heat Transfer
- 15-5** Thermochemical Equations
- 15-6** Standard States and Standard Enthalpy Changes
- 15-7** Standard Molar Enthalpies of Formation, ΔH_f°
- 15-8** Hess's Law
- 15-9** Bond Energies
- 15-10** Changes in Internal Energy, ΔE
- 15-11** Relationship Between ΔH and ΔE

Spontaneity of Physical and Chemical Changes

- 15-12** The Two Aspects of Spontaneity
- 15-13** Dispersal of Energy and Matter
- 15-14** Entropy, S , and Entropy Change, ΔS
- 15-15** The Second Law of Thermodynamics
- 15-16** Free Energy Change, ΔG , and Spontaneity
- 15-17** The Temperature Dependence of Spontaneity

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Understand the terminology of thermodynamics, and the meaning of the signs of changes
- ▶ Use the concept of state functions
- ▶ Carry out calculations of calorimetry to determine changes in energy and enthalpy
- ▶ Use Hess's Law to find the enthalpy change, ΔH , for a reaction from other thermochemical equations with known ΔH values
- ▶ Use Hess's Law to find the standard enthalpy change, ΔH° , for a reaction by using tabulated values of standard molar enthalpies of formation
- ▶ Use Hess's Law to find the molar enthalpy of formation, ΔH_f° , given ΔH° for a reaction and the known molar enthalpies of formation of the other substances in the reaction
- ▶ Use the First Law of Thermodynamics to relate heat, work, and energy changes
- ▶ Relate the work done on or by a system to changes in its volume
- ▶ Use bond energies to estimate heats of reaction for gas phase reactions; use ΔH values for gas phase reactions to find bond energies
- ▶ Understand what is meant by a product-favored (spontaneous) process and by a reactant-favored (nonspontaneous) process
- ▶ Understand the relationship of entropy to the dispersal of energy and dispersal of matter (disorder) in a system
- ▶ Use tabulated values of absolute entropies to calculate the entropy change, ΔS°
- ▶ Understand how the spontaneity of a process is related to entropy changes—the Second Law of Thermodynamics
- ▶ Calculate changes in Gibbs free energy, ΔG , by two methods: (a) from values of ΔH and ΔS and (b) from tabulated values of standard molar free energies of formation; know when to use each type of calculation
- ▶ Use ΔG° to predict whether a process is product-favored (spontaneous) at constant T and P
- ▶ Understand how changes in temperature can affect the spontaneity of a process
- ▶ Predict the temperature range of spontaneity of a chemical or physical process

Energy is very important in every aspect of our daily lives. The food we eat supplies the energy to sustain life with all of its activities and concerns. The availability of relatively inexpensive energy is an important factor in our technological society. This is seen in the costs of fuel, heating and cooling of our homes and workplaces, and electricity to power our lights, appliances, and computers. It is also seen in the costs of goods and services we purchase because a substantial part of the cost of production and delivery is for energy in one form or another. We must understand the scientific basis of the storage and use of energy to learn how to decrease our dependence on consumable oil and natural gas as our main energy sources. Such understanding will have profound ramifications, ranging from our daily lifestyles to international relations.

The concept of energy is at the very heart of science. All physical and chemical processes, including those in all living systems, are accompanied by the transfer of energy. Because energy cannot be created or destroyed, we must understand how to do the “accounting” of energy transfers from one body or one substance to another, or from one form of energy to another.

In **thermodynamics** we study the energy changes that accompany physical and chemical processes. These energy changes usually involve *heat*—hence the “thermo-” part of the term. In this chapter we will study the two main aspects of thermodynamics. The first is **thermochemistry**. This is how we *observe*, *measure*, and *predict* energy changes for both physical changes and chemical reactions. The second part of the chapter will address a more fundamental aspect of thermodynamics. There we will learn to use energy changes to tell whether or not a given process can occur under specified conditions to give predominantly products (or reactants) and how to make a process more (or less) favorable.

▶ Some forms of energy are potential, kinetic, electrical, nuclear, heat, and light.

Heat Changes and Thermochemistry

15-1 The First Law of Thermodynamics

We can define energy as follows.

Energy is the capacity to do work or to transfer heat.

We classify energy into two general types: kinetic and potential. **Kinetic energy** is the energy of motion. The kinetic energy of an object is equal to one half its mass, m , times the square of its velocity, v .

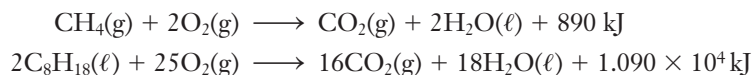
$$E_{\text{kinetic}} = \frac{1}{2} mv^2$$

The heavier a hammer is and the more rapidly it moves, the greater its kinetic energy and the more work it can accomplish.

Potential energy is the energy that a system possesses by virtue of its position or composition. The work that we do to lift an object in a gravitational field is stored in the object as potential energy. If we drop a hammer, its potential energy is converted into kinetic energy as it falls, and it could do work on something it hits—for example, drive a nail or break a piece of glass. Similarly, an electron in an atom has potential energy because of the electrostatic force on it that is due to the positively charged nucleus and the other electrons in that atom and surrounding atoms. Energy can take many other forms: electrical energy, radiant energy (light), nuclear energy, and chemical energy. At the atomic or molecular level, we can think of these as either kinetic or potential energy.

The chemical energy in a fuel or food comes from potential energy stored in atoms due to their arrangements in the molecules. This stored chemical energy can be released when compounds undergo chemical changes, such as those that occur in combustion and metabolism.

Reactions that release energy in the form of heat are called **exothermic** reactions. Combustion reactions of fossil fuels are familiar examples of exothermic reactions. Hydrocarbons—including methane (CH_4), the main component of natural gas, and octane (C_8H_{18}), a minor component of gasoline—undergo combustion with an excess of O_2 to yield CO_2 and H_2O . These reactions release heat energy. The amounts of heat energy released at constant pressure are shown for the reactions of one mole of methane and of two moles of octane.



In such reactions, the total energy of the products is lower than that of the reactants by the amount of energy released, most of which is heat. Some initial activation (e.g., by heat) is needed to get these reactions started. This is shown for CH_4 in Figure 15-1. This activation energy *plus* 890 kJ is released as one mole of $\text{CO}_2(\text{g})$ and two moles of $\text{H}_2\text{O}(\ell)$ are formed.

A process that absorbs energy from its surroundings is called **endothermic**. One such process is shown in Figure 15-2.

Energy changes accompany physical changes, too (see Chapter 13). For example, the melting of one mole of ice at 0°C at constant pressure must be accompanied by the absorption of 6.02 kJ of energy.



This tells us that the total energy of the water is raised by 6.02 kJ in the form of heat during the phase change, even though the temperature remains constant.



© Richard Gross/Corbis

As matter falls from a higher to a lower level, its gravitational potential energy is converted into kinetic energy. A hydroelectric power plant converts the kinetic energy of falling water into electrical (potential) energy.

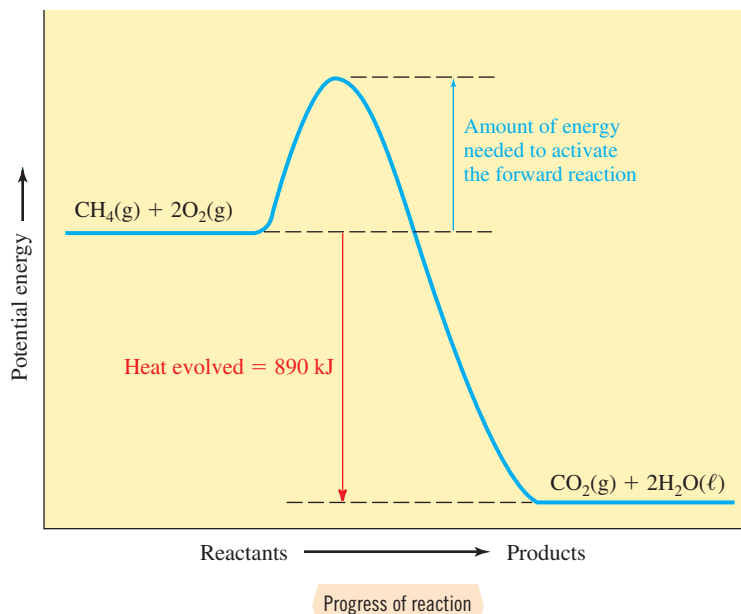
► A hydrocarbon is a binary compound of only hydrogen and carbon. Hydrocarbons may be gaseous, liquid, or solid. All burn.

The amount of heat shown in such an equation always refers to the reaction for the number of moles of reactants and products specified by the coefficients. We call this *one mole of reaction* (even though more than one mole of reactants or products may be shown).

STOP & THINK

It is important to specify the physical states of all substances because different physical states have different energy contents.

Figure 15-1 The difference between the potential energy of the reactants—one mole of $\text{CH}_4(\text{g})$ and two moles of $\text{O}_2(\text{g})$ —and that of the products—one mole of $\text{CO}_2(\text{g})$ and two moles of $\text{H}_2\text{O}(\ell)$ —is the amount of heat evolved in this *exothermic* reaction at constant pressure. For this reaction, it is 890 kJ/mol of reaction. In this chapter, we see how to measure the heat absorbed or released and how to calculate it from other known heat changes. Some initial activation, by heat, for example, is needed to get this reaction started (see Section 16-6). In the absence of such activation energy, a mixture of CH_4 and O_2 can be kept at room temperature for a long time without reacting. For an *endothermic* reaction, the final level is higher than the initial level.



A When solid hydrated barium hydroxide, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, and excess solid ammonium nitrate, NH_4NO_3 , are mixed, an endothermic reaction occurs.

$$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}(\text{s}) + 2\text{NH}_4\text{NO}_3(\text{s}) \longrightarrow \text{Ba}(\text{NO}_3)_2(\text{s}) + 2\text{NH}_3(\text{g}) + 10\text{H}_2\text{O}(\ell)$$

The excess ammonium nitrate dissolves in the water produced in the reaction.



B The dissolution process is also very endothermic. If the flask is placed on a wet wooden block, the water freezes and attaches the block to the flask.

Figure 15-2 An endothermic process.

Some important ideas about energy are summarized in the **First Law of Thermodynamics**.

The combined amount of matter and energy in the universe is constant.

The **Law of Conservation of Energy** is just another statement of the First Law of Thermodynamics.

Energy can never be created nor destroyed in any process. Energy can be transformed into other forms of energy or converted into matter under special circumstances such as nuclear reactions.

15-2 Some Thermodynamic Terms

The substances involved in the chemical and physical changes that we are studying are called the **system**. Everything in the system's environment constitutes its **surroundings**. The **universe** is the system plus its surroundings. The system may be thought of as the part of the universe under investigation. The First Law of Thermodynamics tells us that energy is neither created nor destroyed; it is only transferred between the system and its surroundings.

The **thermodynamic state of a system** is defined by a set of conditions that completely specifies all the properties of the system. This set commonly includes the temperature, pressure, composition (identity and number of moles of each component), and physical state (gas, liquid, or solid) of each part of the system. Once the state has been specified, all other properties—both physical and chemical—are fixed.

The properties of a system—such as P , V , T —are called **state functions**. The *value* of a state function depends only on the state of the system and not on the way in which the system came to be in that state. A *change* in a state function describes a *difference* between the two states. It is independent of the process or pathway by which the change occurs.

For instance, consider a sample of one mole of pure liquid water at 30°C and 1 atm pressure. If at some later time the temperature of the sample is 22°C at the same pressure, then it is in a different thermodynamic state. We can tell that the *net* temperature change is −8°C. It does not matter whether (1) the cooling took place directly (either slowly or rapidly) from 30°C to 22°C, or (2) the sample was first heated to 36°C, then cooled to 10°C, and finally warmed to 22°C, or (3) any other conceivable path was followed from the initial state to the final state. The change in other properties (e.g., the pressure) of the sample is likewise independent of path.

The most important use of state functions in thermodynamics is to describe *changes*. We describe the difference in any quantity, X , as

$$\Delta X = X_{\text{final}} - X_{\text{initial}}$$

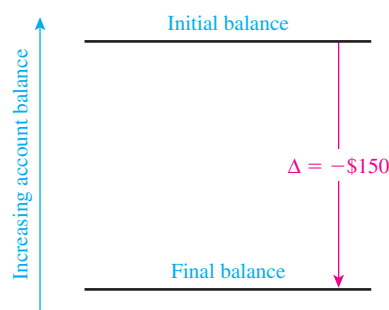
When X increases, the final value is greater than the initial value, so ΔX is *positive*; a decrease in X makes ΔX a *negative* value.

You can consider a state function as analogous to a bank account. With a bank account, at any time you can measure the amount of money in your account (your balance) in convenient terms—dollars and cents. Changes in this balance can occur for several reasons, such as deposit of your paycheck, writing of checks, or service charges assessed by the bank. In our analogy these transactions are *not* state functions, but they do cause *changes* in the state function (the balance in the account). You can think of the bank balance on a vertical scale; a deposit of \$150 changes the balance by +\$150, no matter what it was at the start, just as a withdrawal of \$150 would change the balance by −\$150. Similarly, we shall see that the energy of a system is a state function that can be changed—for instance, by an energy “deposit” of heat absorbed or work done on the system, or by an energy “withdrawal” of heat given off or work done by the system.

We can describe *differences* between levels of a state function, regardless of where the zero level is located. In the case of a bank balance, the “natural” zero level is obviously the point at which we open the account, before any deposits or withdrawals. In contrast, the zero levels on most temperature scales are set arbitrarily. When we say that the temperature of an ice–water mixture is “zero degrees Celsius,” we are not saying that the mixture contains no temperature! We have simply chosen to describe this point on the temperature scale by the number *zero*; conditions of higher temperature are described by positive temperature values, and those of lower temperature have negative values, “below zero.” The phrase “15 degrees cooler” has the same meaning anywhere on the scale. Many of the scales that we use in thermodynamics are arbitrarily defined in this way. Arbitrary scales are useful when we are interested only in *changes* in the quantity being described.

Any property of a system that depends only on the values of its state functions is also a state function. For instance, the volume of a given sample of water depends only on tem-

► State functions are represented by capital letters. Here P refers to pressure, V to volume, and T to absolute temperature.



Here is a graphical representation of a \$150 decrease in your bank balance. We express the change in your bank balance as $\Delta\$ = \$_{\text{final}} - \$_{\text{initial}}$. Your final balance is *less* than your initial balance, so the result is *negative*, indicating a *decrease*. There are many ways to get this same net change—one large withdrawal or some combination of deposits, withdrawals, interest earned, and service charges. All of the Δ values we will see in this chapter can be thought of in this way.

Unless otherwise noted, all content on this page is © Cengage Learning.

perature, pressure, and physical state; therefore, volume is a state function. We shall encounter other thermodynamic state functions.

15-3 Enthalpy Changes

Most chemical reactions and physical changes occur at constant (usually atmospheric) pressure.

► The symbol q represents the amount of heat absorbed by the system. The subscript p indicates a constant-pressure process.

The quantity of heat transferred into or out of a system as it undergoes a chemical or physical change at constant pressure, q_p , is defined as the **enthalpy change, ΔH** , of the process.

An enthalpy change is sometimes loosely referred to as a *heat change* or a *heat of reaction*. The enthalpy change is equal to the enthalpy or “heat content,” H , of the substances produced minus the enthalpy of the substances consumed.

$$\Delta H = H_{\text{final}} - H_{\text{initial}} \quad \text{or} \quad \Delta H = H_{\text{substances produced}} - H_{\text{substances consumed}}$$

It is impossible to know the absolute enthalpy (heat content) of a system. *Enthalpy is a state function*, however, and it is the *change in enthalpy* in which we are interested; this can be measured for many processes. In the next several sections, we focus on chemical reactions and the enthalpy changes that occur in these processes. We first discuss the experimental determination of enthalpy changes.

15-4 Calorimetry: Measurement of Heat Transfer

We can determine the energy change associated with a chemical or physical process by using an experimental technique called *calorimetry*. This technique is based on observing the temperature change when a system absorbs or releases energy in the form of heat. The experiment is carried out in a device called a **calorimeter**, in which the temperature change of a known amount of substance (often water) of known specific heat is measured. The temperature change is caused by the absorption or release of heat by the chemical or physical process under study.

► A review of calculations involved with heat transfer (see Sections 1-14, 13-9, and 13-11) will help you understand this section.

► The polystyrene insulation of the simple coffee-cup calorimeter ensures that little heat escapes from or enters the container.

A “coffee-cup” calorimeter (Figure 15-3) is often used in laboratory classes to measure “heats of reaction” at constant pressure, q_p , in aqueous solutions. Reactions are chosen so that there are no gaseous reactants or products. Thus, all reactants and products remain in the vessel throughout the experiment. Such a calorimeter could be used to measure the amount of heat absorbed or released when a reaction takes place in aqueous solution. We can consider the reactants and products as the system and the calorimeter plus the solution (mostly water) as the surroundings. For an exothermic reaction, the amount of heat evolved by the reaction can be calculated from the amount by which it causes the temperature of the calorimeter and the solution to rise. The heat can be visualized as divided into two parts.

$$\left(\begin{array}{c} \text{amount of heat} \\ \text{released by reaction} \end{array} \right) = \left(\begin{array}{c} \text{amount of heat absorbed} \\ \text{by calorimeter} \end{array} \right) + \left(\begin{array}{c} \text{amount of heat} \\ \text{absorbed by solution} \end{array} \right)$$

The amount of heat absorbed by a calorimeter is sometimes expressed as the *heat capacity* of the calorimeter, in joules per degree. The heat capacity of a calorimeter is determined by adding a known amount of heat and measuring the rise in temperature of the calorimeter and of the solution it contains. This heat capacity of a calorimeter is sometimes called its *calorimeter constant*.

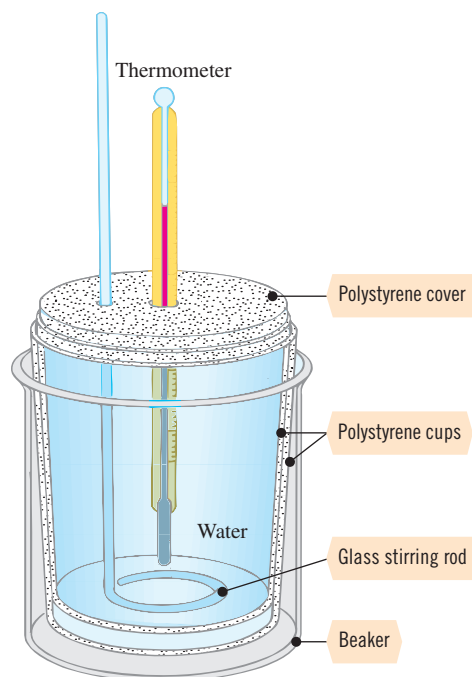


Figure 15-3 A coffee-cup calorimeter. The stirring rod is moved up and down to ensure thorough mixing and uniform heating of the solution during reaction. The polystyrene walls and top provide insulation so that very little heat escapes. This kind of calorimeter measures q_p , the heat transfer due to a reaction occurring at constant pressure.

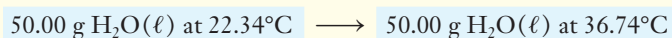
EXAMPLE 15-1 Heat Capacity of a Calorimeter

We add 3.358 kJ of heat to a calorimeter that contains 50.00 g of water. The temperature of the water and the calorimeter, originally at 22.34°C, increases to 36.74°C. Calculate the heat capacity of the calorimeter in J/°C. The specific heat of water is 4.184 J/g · °C.

Plan

We first calculate the amount of heat gained by the water in the calorimeter. The rest of the heat must have been gained by the calorimeter, so we can determine the heat capacity of the calorimeter.

Solution



The temperature change is $(36.74 - 22.34)^\circ\text{C} = 14.40^\circ\text{C}$.

$$q_{\text{J}} = 50.00 \text{ g} \times \frac{4.184 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times 14.40^\circ\text{C} = 3.012 \times 10^3 \text{ J}$$

The total amount of heat added was 3.358 kJ or $3.358 \times 10^3 \text{ J}$. The difference between these heat values is the amount of heat absorbed by the calorimeter.

$$q_{\text{J}} = 3.358 \times 10^3 \text{ J} - 3.012 \times 10^3 \text{ J} = 0.346 \times 10^3 \text{ J}, \text{ or } 346 \text{ J absorbed by the calorimeter}$$

To obtain the heat capacity of the calorimeter, we divide the amount of heat absorbed by the calorimeter, 346 J, by its temperature change.

$$C_{\text{J}/^\circ\text{C}} = \frac{346 \text{ J}}{14.40^\circ\text{C}} = 24.0 \text{ J}/^\circ\text{C}$$

The calorimeter absorbs 24.0 J of heat for each degree Celsius increase in its temperature.

You should now work Exercise 60.

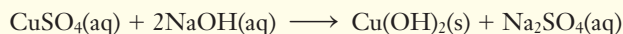
► One way to add a measurable amount of heat is to use an electric heater.

STOP & THINK

Note that, because we are using the *change* in temperature (ΔT) in this example, temperatures can be expressed as °C or K. That is because the magnitude of a change of 1°C is equal to 1 K. In this problem $\Delta T = 14.40^\circ\text{C} = 14.40 \text{ K}$. But, when working with mathematical equations that use absolute temperatures T (not ΔT !), it is important to express temperatures in kelvins. In this chapter, we will see mathematical formulas that use T and ΔT , so it is important to keep track of which is being used.

EXAMPLE 15-2 Heat Measurements Using a Calorimeter

A 50.0-mL sample of 0.400 *M* copper(II) sulfate solution at 23.35°C is mixed with 50.0 mL of 0.600 *M* sodium hydroxide solution, also at 23.35°C, in the coffee-cup calorimeter of Example 15-1. After the reaction occurs, the temperature of the resulting mixture is measured to be 25.23°C. The density of the final solution is 1.02 g/mL. Calculate the amount of heat evolved. Assume that the specific heat of the solution is the same as that of pure water, 4.184 J/g · °C.



Plan

The amount of heat released by the reaction is absorbed by the calorimeter *and* by the solution. To find the amount of heat absorbed by the solution, we must know the mass of solution; to find that, we assume that the volume of the reaction mixture is the sum of the volumes of the original solutions.

Solution

The mass of solution is

$$\underline{?} \text{ g soln} = (50.0 + 50.0) \text{ mL} \times \frac{1.02 \text{ g soln}}{\text{mL}} = 102 \text{ g soln}$$

The amount of heat absorbed by the calorimeter *plus* the amount absorbed by the solution is

$$\begin{aligned} \underline{?} \text{ J} &= \overbrace{\frac{24.0 \text{ J}}{^\circ\text{C}} \times (25.23 - 23.35)^\circ\text{C}}^{\text{amount of heat absorbed by calorimeter}} + \overbrace{102 \text{ g} \times \frac{4.18 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times (25.23 - 23.35)^\circ\text{C}}^{\text{amount of heat absorbed by solution}} \\ &= 45 \text{ J} + 801 \text{ J} = 846 \text{ J absorbed by solution plus calorimeter} \end{aligned}$$

Thus, the reaction must have liberated 846 J, or 0.846 kJ, of heat.

You should now work Exercise 64(a).

► When dilute aqueous solutions are mixed, their volumes are very nearly additive.

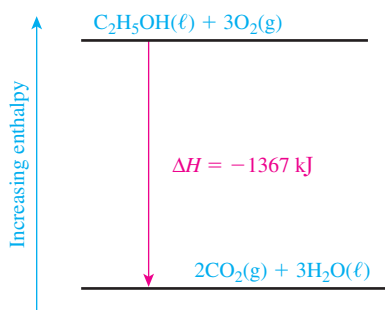


Charles D. Winters



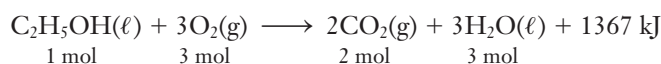
Charles D. Winters

The heat released by the reaction of HCl(aq) with NaOH(aq) causes the temperature of the solution to rise.



15-5 Thermochemical Equations

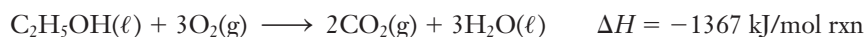
A balanced chemical equation, written together with a description of the corresponding heat change, is called a **thermochemical equation**. For example,



is a thermochemical equation that describes the combustion (burning) of one mole of liquid ethanol at a particular temperature and pressure. The coefficients in a balanced thermochemical equation *must* be interpreted as *numbers of moles* of each reactant and product. Thus, 1367 kJ of heat is released when *one* mole of C₂H₅OH(ℓ) reacts with *three* moles of O₂(g) to give *two* moles of CO₂(g) and *three* moles of H₂O(ℓ). We refer to this amount of reaction as one **mole of reaction**, which we abbreviate “mol rxn.” This interpretation allows us to write various unit factors as desired.

$$\frac{1 \text{ mol C}_2\text{H}_5\text{OH}(\ell)}{1 \text{ mol rxn}}, \frac{2 \text{ mol CO}_2(\text{g})}{1 \text{ mol rxn}}, \frac{1367 \text{ kJ of heat released}}{1 \text{ mol rxn}}, \text{ and so on}$$

The thermochemical equation is more commonly written as



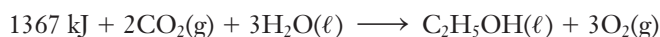
The negative sign indicates that this is an *exothermic* reaction (i.e., it gives *off* heat).

We always interpret ΔH as the enthalpy change for the reaction as written; that is, as (enthalpy change)/(mole of reaction), where “mole of reaction” means “for the number of moles of each substance shown by the coefficients in the balanced equation.”

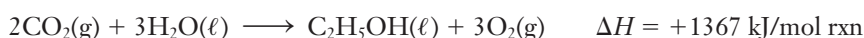
We can then use several unit factors to interpret this thermochemical equation.

$$\begin{aligned}\frac{1367 \text{ kJ given off}}{\text{mol of reaction}} &= \frac{1367 \text{ kJ given off}}{\text{mol C}_2\text{H}_5\text{OH}(\ell) \text{ consumed}} = \frac{1367 \text{ kJ given off}}{3 \text{ mol O}_2(\text{g}) \text{ consumed}} \\ &= \frac{1367 \text{ kJ given off}}{2 \text{ mol CO}_2(\text{g}) \text{ formed}} = \frac{1367 \text{ kJ given off}}{3 \text{ mol H}_2\text{O}(\ell) \text{ formed}}\end{aligned}$$

The reverse reaction would require the absorption of 1367 kJ under the same conditions.



That is, it is *endothermic*, with $\Delta H = +1367 \text{ kJ}$.

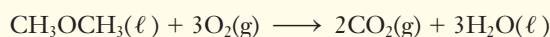


It is important to remember the following conventions regarding thermochemical equations:

1. The coefficients in a balanced thermochemical equation refer to the numbers of *moles* of reactants and products involved. In the thermodynamic interpretation of equations, we *never* interpret the coefficients as *numbers of molecules*. Thus, it is acceptable to write coefficients as fractions rather than as integers, when convenient. But most chemists prefer to use the smallest integer values for the coefficients.
2. The numerical value of ΔH (or any other thermodynamic change) is specific to the *number of moles* of substances specified by the balanced equation. This amount of change is called *one mole of reaction*, so we can express ΔH in units of energy/mol rxn. For brevity, the units of ΔH are sometimes written kJ/mol or even just kJ. No matter what units are used, be sure that you interpret the thermodynamic change *per mole of reaction for the balanced chemical equation to which it refers*. If a different amount of material is involved in the reaction, then the ΔH (or other change) must be scaled accordingly.
3. The physical states of all species are important and must be specified. Heat is given off or absorbed when phase changes occur, so different amounts of heat could be involved in a reaction depending on the phases of reactants and products.
4. The value of ΔH usually does not change significantly with moderate changes in temperature.

EXAMPLE 15-3 Thermochemical Equations

When 2.61 grams of dimethyl ether, CH_3OCH_3 , is burned at constant pressure, 82.5 kJ of heat is given off. Find ΔH for the reaction



Plan

We scale the amount of heat given off in the experiment to correspond to the amount of CH_3OCH_3 shown in the balanced equation.

► To interpret what a value of ΔH means, we must know the balanced chemical equation to which it refers.



NASA/Tony Gray and Tom Farrar

The launch of the space shuttle requires about 2×10^{10} kilojoules of energy. About one-sixth of this comes from the reaction of hydrogen, H_2 , and oxygen, O_2 . The rest comes from the explosive decomposition of ammonium perchlorate, NH_4ClO_4 , in solid-fuel rockets. The final launch was on July 8, 2011, by the shuttle Atlantis.

Unless otherwise noted, all content on this page is © Cengage Learning.

STOP & THINK

The value of ΔH must be scaled to correspond to a particular amount of reaction, described by the balanced thermochemical equation.

Solution

$$\frac{? \text{ kJ given off}}{\text{mol rxn}} = \frac{82.5 \text{ kJ given off}}{2.61 \text{ g CH}_3\text{OCH}_3} \times \frac{46.0 \text{ g CH}_3\text{OCH}_3}{\text{mol CH}_3\text{OCH}_3} \times \frac{1 \text{ mol CH}_3\text{OCH}_3}{\text{mol rxn}}$$

$$= 1450 \text{ kJ/mol rxn}$$

Because heat is given off, we know that the reaction is exothermic so the value of ΔH should be negative.

$$\Delta H = -1450 \text{ kJ/mol rxn}$$

You should now work Exercise 21.

EXAMPLE 15-4 Thermochemical Equations

Write the thermochemical equation for the reaction in Example 15-2.

Plan

We must determine *how much* reaction occurred—that is, how many moles of reactants were consumed. We first multiply the volume, in liters, of each solution by its concentration in mol/L (molarity) to determine the number of moles of each reactant mixed. Then we identify the limiting reactant. We scale the amount of heat released in the experiment to correspond to the number of moles of that reactant shown in the balanced equation.

Solution

Using the data from Example 15-2,

$$? \text{ mol CuSO}_4 = 0.0500 \text{ L} \times \frac{0.400 \text{ mol CuSO}_4}{1.00 \text{ L}} = 0.0200 \text{ mol CuSO}_4$$

$$? \text{ mol NaOH} = 0.0500 \text{ L} \times \frac{0.600 \text{ mol NaOH}}{1.00 \text{ L}} = 0.0300 \text{ mol NaOH}$$

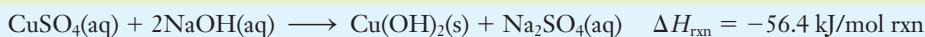
We determine which is the limiting reactant (review Section 3-3).

Required Ratio	Available Ratio
$\frac{1 \text{ mol CuSO}_4}{2 \text{ mol NaOH}} = \frac{0.500 \text{ mol CuSO}_4}{1.00 \text{ mol NaOH}}$	$\frac{0.0200 \text{ mol CuSO}_4}{0.0300 \text{ mol NaOH}} = \frac{0.667 \text{ mol CuSO}_4}{1.00 \text{ mol NaOH}}$

More CuSO_4 is available than is required to react with the NaOH . Thus, 0.846 kJ of heat was given off during the consumption of 0.0300 mol of NaOH . The amount of heat given off per “mole of reaction” is

$$\frac{? \text{ kJ released}}{\text{mol rxn}} = \frac{0.846 \text{ kJ given off}}{0.0300 \text{ mol NaOH}} \times \frac{2 \text{ mol NaOH}}{\text{mol rxn}} = \frac{56.4 \text{ kJ given off}}{\text{mol rxn}}$$

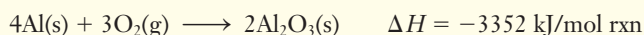
Thus, when the reaction occurs *to the extent indicated by the balanced chemical equation*, 56.4 kJ is released. Remembering that exothermic reactions have negative values of ΔH_{rxn} , we write



You should now work Exercise 64(b).

EXAMPLE 15-5 Amount of Heat Produced

When aluminum metal is exposed to atmospheric oxygen (as in aluminum doors and windows), it is oxidized to form aluminum oxide. How much heat is released by the complete oxidation of 24.2 grams of aluminum at 25°C and 1 atm? The thermochemical equation is



► NaOH is the limiting reactant.

STOP & THINK

Write complete units, including substance formulas. Then remember to scale the heat change to the amount of reaction described in the balanced thermochemical equation. Heat is released, so this is an exothermic reaction and has a negative value of ΔH_{rxn} .

Plan

The thermochemical equation tells us that 3352 kJ of heat is released for every mole of reaction, that is, for every 4 moles of Al that reacts. We convert 24.2 g of Al to moles and then calculate the number of kilojoules corresponding to that number of moles of Al, using the unit factors

$$\frac{-3352 \text{ kJ}}{\text{mol rxn}} \quad \text{and} \quad \frac{1 \text{ mol rxn}}{4 \text{ mol Al}}$$

Solution

For 24.2 g Al,

$$\Delta H \text{ kJ} = 24.2 \text{ g Al} \times \frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \times \frac{1 \text{ mol rxn}}{4 \text{ mol Al}} \times \frac{-3352 \text{ kJ}}{\text{mol rxn}} = -751 \text{ kJ}$$

This tells us that 751 kJ of heat is released to the surroundings during the oxidation of 24.2 grams of aluminum.

You should now work Exercises 16 and 17.

STOP & THINK

The *sign* tells us that heat was released, but it would be grammatical nonsense to say in words that “–751 kJ of heat was released.” As an analogy, suppose you give your friend \$5. Your $\Delta \$$ is –\$5, but in describing the transaction you would not say “I gave her minus five dollars.” Instead, you would say, “I gave her five dollars.”

**Problem-Solving Tip** Mole of Reaction

Remember that a thermochemical equation can have *different* coefficients (numbers of moles) of *different* reactants or products, which need not equal one. In Example 15-5 one mole of reaction corresponds to 4 moles of Al(s), 3 moles of O₂(g), and 2 moles of Al₂O₃(s).

15-6 Standard States and Standard Enthalpy Changes

The **thermodynamic standard state** of a substance is its most stable pure form under standard pressure (one atmosphere)* and at some specific temperature (25°C or 298 K unless otherwise specified). Examples of elements in their standard states at 25°C are hydrogen, gaseous diatomic molecules, H₂(g); mercury, a silver-colored liquid metal, Hg(*ℓ*); sodium, a silvery-white solid metal, Na(s); and carbon, a grayish-black solid called graphite, C(graphite). We use C(graphite) instead of C(s) to distinguish it from other solid forms of carbon, such as C(diamond). The reaction C(diamond) → C(graphite) would be *exothermic* by 1.897 kJ/mol rxn; C(graphite) is thus more stable than C(diamond). Examples of standard states of compounds include ethanol (ethyl alcohol or grain alcohol), a liquid, C₂H₅OH(*ℓ*); water, a liquid, H₂O(*ℓ*); calcium carbonate, a solid, CaCO₃(s); and carbon dioxide, a gas, CO₂(g). Keep in mind the following conventions for thermochemical standard states.

1. For a *pure* substance in the liquid or solid phase, the standard state is the pure liquid or solid.
2. For a gas, the standard state is the gas at a pressure of *one atmosphere*; in a mixture of gases, its partial pressure must be one atmosphere.
3. For a substance in solution, the standard state refers to *one-molar* concentration.

For ease of comparison and tabulation, we often refer to thermochemical or thermodynamic changes “at standard states” or, more simply, to a *standard change*. To indicate a change at standard pressure, we add a superscript zero, which is read as “naught.” If some temperature other than the standard temperature of 25°C (298 K) is specified, we indicate it with a subscript; if no subscript appears, a temperature of 25°C (298 K) is implied.

*IUPAC has changed the standard pressure from 1 atm to 1 bar. Because 1 bar is equal to 0.987 atm, the differences in thermodynamic calculations are negligible except in work of very high precision. Many tables of thermodynamic data are still based on a standard pressure of 1 atm, so we use that pressure in this text.

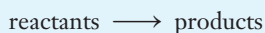
► A temperature of 25°C is 77°F. This is slightly above typical room temperature. Notice that these thermodynamic “standard conditions” are not the same as the “standard temperature and pressure (STP)” that we used in gas calculations involving standard molar volume (see Chapter 12).

► If the substance exists in several different forms, the form that is most stable at 25°C and 1 atm is the standard state.

► For gas laws (see Chapter 12), standard temperature is taken as 0°C. For thermodynamics, it is taken as 25°C.

► This is sometimes referred to as the *standard heat of reaction*. We verbally refer to this as “delta H naught reaction.”

The **standard enthalpy change**, ΔH_{rxn}^0 , for a reaction



refers to the ΔH when the specified number of moles of reactants, all at standard states, are converted *completely* to the specified number of moles of products, all at standard states.

We allow a reaction to take place, with changes in temperature or pressure if necessary; when the reaction is complete, we return the products to the same conditions of temperature and pressure that we started with, *keeping track of energy or enthalpy changes* as we do so. When we describe a process as taking place “at constant T and P ,” we mean that the initial and final conditions are the same. Because we are dealing with changes in state functions, the net change is the same as the change we would have obtained hypothetically with T and P actually held constant.

15-7 Standard Molar Enthalpies of Formation, ΔH_f^0

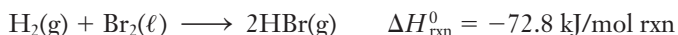
It is not possible to determine the total enthalpy content of a substance on an absolute scale. Because we need to describe only *changes* in this state function, we can define an *arbitrary scale* as follows.

► We can think of ΔH_f^0 as the enthalpy content of each substance, in its standard state, relative to the enthalpy content of the elements, in their standard states. This is why ΔH_f^0 for an element in its standard state is zero.

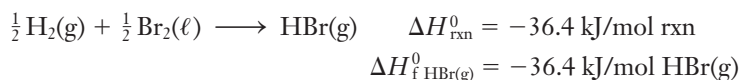
The **standard molar enthalpy of formation**, ΔH_f^0 , of a substance is the enthalpy change for the reaction in which *one mole* of the substance in a specified state is formed from its elements in their standard states. By convention, the ΔH_f^0 value for any *element in its standard state* is defined as zero.

Standard molar enthalpy of formation is often called **standard molar heat of formation** or, more simply, **heat of formation**. The superscript zero in ΔH_f^0 signifies standard pressure, 1 atmosphere. Negative values for ΔH_f^0 describe exothermic formation reactions, whereas positive values for ΔH_f^0 describe endothermic formation reactions.

The enthalpy change for a balanced equation that gives a compound from its elements does not necessarily give a molar enthalpy of formation for the compound. Consider the following exothermic reaction at standard conditions.



We see that *two* moles of HBr(g) are formed in the reaction as written. Half as much energy, 36.4 kJ, is liberated when *one mole* of HBr(g) is produced from its constituent elements in their standard states. For HBr(g), $\Delta H_f^0 = -36.4 \text{ kJ/mol}$. This can be shown by dividing all coefficients in the balanced equation by 2.



► The coefficients $\frac{1}{2}$ preceding $\text{H}_2(\text{g})$ and $\text{Br}_2(\ell)$ do *not* imply half a molecule of each. In thermochemical equations, the coefficients always refer to the number of *moles* under consideration.

Standard heats of formation of some common substances are tabulated in Table 15-1. Appendix K contains a more extensive listing.

When referring to a thermodynamic quantity for a *substance*, we often omit the description of the substance from the units. Units for tabulated ΔH_f^0 values are given as “kJ/mol”; we must interpret this as “per mole of the substance in the specified state.” For instance, for HBr(g) the tabulated ΔH_f^0 value of -36.4 kJ/mol should be interpreted as $\frac{-36.4 \text{ kJ}}{\text{mol HBr(g)}}$.

Table 15-1 Selected Standard Molar Enthalpies of Formation at 298 K

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
Br ₂ (ℓ)	0	HgS(s) red	-58.2
Br ₂ (g)	30.91	H ₂ (g)	0
C(diamond)	1.897	HBr(g)	-36.4
C(graphite)	0	H ₂ O(ℓ)	-285.8
CH ₄ (g)	-74.81	H ₂ O(g)	-241.8
C ₂ H ₄ (g)	52.26	NO(g)	90.25
C ₆ H ₆ (ℓ)	49.03	Na(s)	0
C ₂ H ₅ OH(ℓ)	-277.7	NaCl(s)	-411.0
CO(g)	-110.5	O ₂ (g)	0
CO ₂ (g)	-393.5	SO ₂ (g)	-296.8
CaO(s)	-635.5	SiH ₄ (g)	34.0
CaCO ₃ (s)	-1207.0	SiCl ₄ (g)	-657.0
Cl ₂ (g)	0	SiO ₂ (s)	-910.9

STOP & THINK

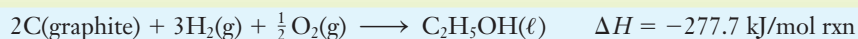
The ΔH_f° values of Br₂(g) and C(diamond) are *not equal to 0* at 298 K. This is because the standard states of these elements are Br₂(ℓ) and C(graphite), respectively.

EXAMPLE 15-6 Interpretation of ΔH_f°

The standard molar enthalpy of formation of ethanol, C₂H₅OH(ℓ), is -277.7 kJ/mol. Write the thermochemical equation for the reaction for which $\Delta H_{\text{rxn}}^\circ = -277.7$ kJ/mol rxn.

Plan

The definition of ΔH_f° of a substance refers to a reaction in which *one mole* of the substance in a specified state is formed from the elements *in their standard states*. We put one mole of C₂H₅OH(ℓ) on the right side of the chemical equation and put the appropriate elements in their standard states on the left. We balance the equation *without changing the coefficient of the product*, even if we must use fractional coefficients on the left.

Solution

You should now work Exercise 28.

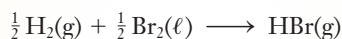
Problem-Solving Tip How Do We Interpret Fractional Coefficients?

Remember that we *always* interpret the coefficients in thermochemical equations as numbers of *moles* of reactants or products. The $\frac{1}{2}\text{O}_2(\text{g})$ in the answer to Example 15-6 refers to $\frac{1}{2}$ *mole* of O₂ molecules, or

$$\frac{1}{2} \text{ mol O}_2 \times \frac{32.0 \text{ g O}_2}{\text{mol O}_2} = 16.0 \text{ g O}_2$$

It is important to realize that this is *not* the same as one mole of O atoms (though that would also weigh 16.0 g).

Similarly, the fractional coefficients in



refer to

$$\frac{1}{2} \text{ mol H}_2 \times \frac{2.0 \text{ g H}_2}{\text{mol H}_2} = 1.0 \text{ g H}_2$$

and

$$\frac{1}{2} \text{ mol Br}_2 \times \frac{159.8 \text{ g Br}_2}{\text{mol Br}_2} = 79.9 \text{ g Br}_2$$

respectively.

15-8 Hess's Law

In 1840, G. H. Hess (1802–1850) published his **law of heat summation**, which he derived on the basis of numerous thermochemical observations.

The enthalpy change for a reaction is the same whether it occurs by one step or by any series of steps.

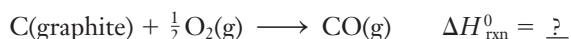
► As an analogy, consider traveling from Kansas City (elevation 884 ft above sea level) to Denver (elevation 5280 ft). The change in elevation is $(5280 - 884) \text{ ft} = 4396 \text{ ft}$, regardless of the route taken.

Enthalpy is a state function. Its *change* is therefore independent of the pathway by which a reaction occurs. We do not need to know whether the reaction *does*, or even *can*, occur by the series of steps used in the calculation. The steps must (if only “on paper”) result in the overall reaction. Hess's Law lets us calculate enthalpy changes for reactions for which the changes could be measured only with difficulty, if at all. In general terms, Hess's Law of heat summation may be represented as

$$\Delta H_{\text{rxn}}^0 = \Delta H_{\text{a}}^0 + \Delta H_{\text{b}}^0 + \Delta H_{\text{c}}^0 + \cdots$$

Here a, b, c, . . . refer to balanced thermochemical equations that can be summed to give the equation for the desired reaction.

Consider the following reaction.

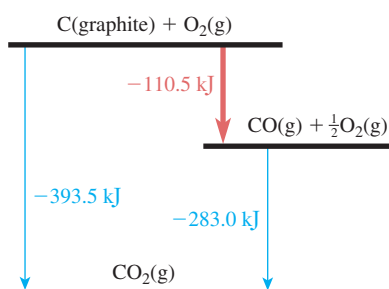


The enthalpy change for this reaction cannot be measured directly. Even though CO(g) is the predominant product of the reaction of graphite with a *limited* amount of O₂(g), some CO₂(g) is always produced as well. The following reactions do go to completion with excess O₂(g); therefore, ΔH^0 values have been measured experimentally for them. [Pure CO(g) is readily available.]

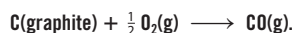


► You are familiar with the addition and subtraction of algebraic equations. This method of combining thermochemical equations is analogous.

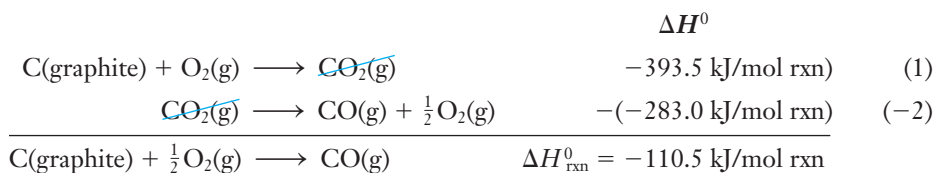
We can “work backward” to find out how to combine these two known equations to obtain the desired equation. We want one mole of CO on the right, so we reverse equation (2) [designated below as (–2)]; heat is then absorbed instead of released, so we must change the sign of its ΔH^0 value. Then we add it to equation (1), canceling equal numbers of moles of the same species on each side. This gives the equation for the reaction we want. Adding the corresponding enthalpy changes gives the enthalpy change we seek.



Above is a schematic representation of the enthalpy changes for the reaction



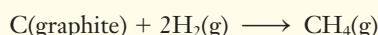
The ΔH value for each step is based on the number of moles of each substance indicated.

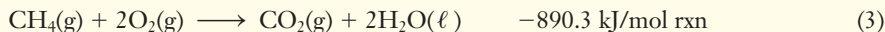


This equation shows the formation of one mole of CO(g) in its standard state from the elements in their standard states. In this way, we determine that ΔH_f^0 for CO(g) is –110.5 kJ/mol.

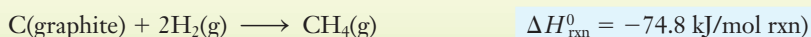
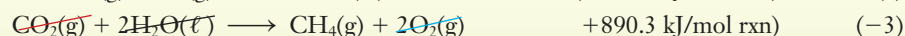
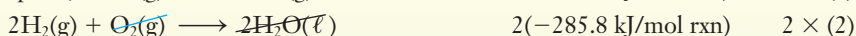
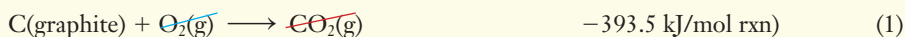
EXAMPLE 15-7 Combining Thermochemical Equations: Hess's Law

Use the thermochemical equations shown here to determine ΔH_{rxn}^0 at 25°C for the following reaction.



ΔH° **Plan**

- (i) We want one mole of C(graphite) as overall reactant, so we write down thermochemical equation (1).
- (ii) We want two moles of H₂(g) as overall reactants, so we multiply thermochemical equation (2) by 2 [designated below as 2 × (2)].
- (iii) We want one mole of CH₄(g) as overall product, so we reverse thermochemical equation (3) to give (−3).
- (iv) Then we add these thermochemical equations term by term. The result is the desired thermochemical equation, with all unwanted substances canceling. The sum of the ΔH° values is the ΔH° for the desired reaction.

Solution ΔH° 

CH₄(g) cannot be formed directly from C(graphite) and H₂(g), so its ΔH°_f value cannot be measured directly. The result of this example tells us that this value is −74.8 kJ/mol.

► These are combustion reactions, for which $\Delta H^\circ_{\text{rxn}}$ values can be readily determined from calorimetry experiments.

STOP & THINK

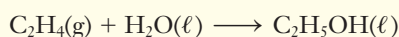
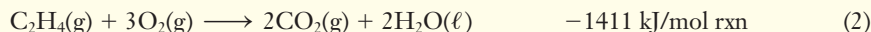
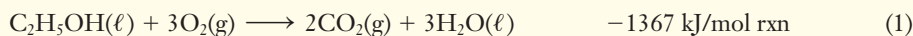
Remember that multiplying a thermochemical equation also multiplies its ΔH° by the same factor. Reversing a thermochemical equation changes the sign of its ΔH° .

STOP & THINK

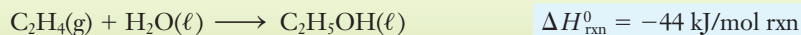
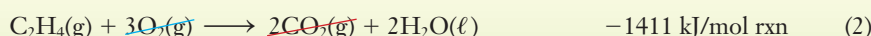
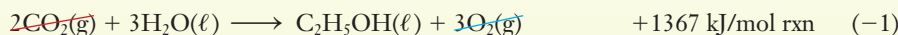
We have used a series of reactions for which ΔH° values can be easily measured to calculate ΔH° for a reaction that cannot be carried out.

EXAMPLE 15-8 Combining Thermochemical Equations: Hess's Law

Given the following thermochemical equations, calculate the heat of reaction at 298 K for the reaction of ethylene with water to form ethanol.

 ΔH° **Plan**

We reverse equation (1) to give (−1); when the equation is reversed, the sign of ΔH° is changed because the reverse of an exothermic reaction is endothermic. Then we add the thermochemical equations.

Solution ΔH° 

You should now work Exercises 32 and 34.

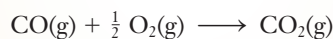
STOP & THINK

If you reverse a chemical equation, remember to switch the sign of its $\Delta H^\circ_{\text{rxn}}$.

Problem Solving Tip ΔH_f° Refers to a Specific Reaction

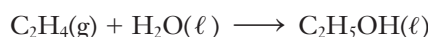
The ΔH° for the reaction in Example 15-8 is -44 kJ for each mole of $\text{C}_2\text{H}_5\text{OH}(\ell)$ formed. This reaction, however, does *not* involve formation of $\text{C}_2\text{H}_5\text{OH}(\ell)$ *from its constituent elements* because C_2H_4 and H_2O are not elements; therefore, $\Delta H_{\text{rxn}}^\circ$ is *not* ΔH_f° for $\text{C}_2\text{H}_5\text{OH}(\ell)$. We have seen the reaction for ΔH_f° of $\text{C}_2\text{H}_5\text{OH}(\ell)$ in Example 15-6.

Similarly, the $\Delta H_{\text{rxn}}^\circ$ for

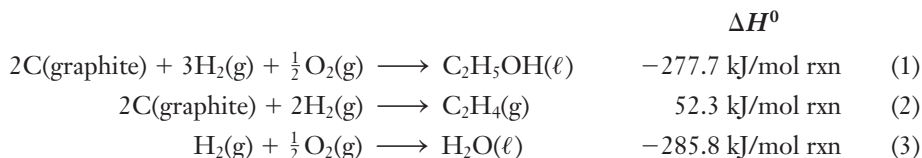


is *not* ΔH_f° for $\text{CO}_2(\text{g})$.

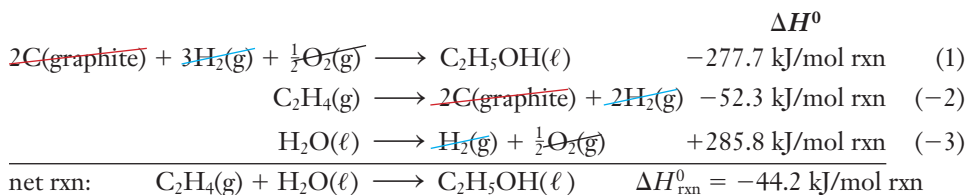
Another interpretation of Hess's Law lets us use tables of ΔH_f° values to calculate the enthalpy change for a reaction. Let us consider again the reaction of Example 15-8.



A table of ΔH_f° values (see Appendix K) gives $\Delta H_{\text{f C}_2\text{H}_5\text{OH}(\ell)}^\circ = -277.7 \text{ kJ/mol}$, $\Delta H_{\text{f C}_2\text{H}_4(\text{g})}^\circ = 52.3 \text{ kJ/mol}$, and $\Delta H_{\text{f H}_2\text{O}(\ell)}^\circ = -285.8 \text{ kJ/mol}$. We may express this information in the form of the following thermochemical equations.



We may generate the equation for the desired net reaction by adding equation (1) to the reverse of equations (2) and (3). The value of ΔH° for the desired reaction is then the sum of the corresponding ΔH° values.



We see that ΔH° for this reaction is given by

$$\Delta H_{\text{rxn}}^\circ = \Delta H_{(1)}^\circ + \Delta H_{(-2)}^\circ + \Delta H_{(-3)}^\circ$$

or by

$$\Delta H_{\text{rxn}}^\circ = \Delta H_{\text{f C}_2\text{H}_5\text{OH}(\ell)}^\circ - [\Delta H_{\text{f C}_2\text{H}_4(\text{g})}^\circ + \Delta H_{\text{f H}_2\text{O}(\ell)}^\circ]$$

product
reactants

In general terms this is a very useful form of Hess's Law.

$$\Delta H_{\text{rxn}}^\circ = \sum n \Delta H_{\text{f products}}^\circ - \sum n \Delta H_{\text{f reactants}}^\circ$$

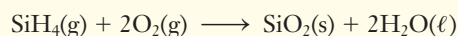
The standard enthalpy change of a reaction is equal to the sum of the standard molar enthalpies of formation of the products, each multiplied by its coefficient, n , in the *balanced equation*, minus the corresponding sum of the standard molar enthalpies of formation of the reactants.

► The capital Greek letter sigma (Σ) is read "the sum of." The Σn means that the ΔH_f° value of each product and reactant must be multiplied by its coefficient, n , in the balanced equation. The resulting values are then added.

In effect this form of Hess's Law supposes that the reaction occurs by converting reactants to the elements in their standard states, then converting these to products (Figure 15-4). Few, if any, reactions actually occur by such a pathway. Nevertheless, because H is a state function the ΔH^0 for this *hypothetical* pathway for *reactants* $\longrightarrow$ *products* would be the same as that for any other pathway—including the one by which the reaction actually occurs.

EXAMPLE 15-9 Using ΔH_f^0 Values: Hess's Law

Calculate ΔH_{rxn}^0 for the following reaction at 298 K.



Plan

We apply Hess's Law in the form $\Delta H_{\text{rxn}}^0 = \sum n \Delta H_f^0 \text{ products} - \sum n \Delta H_f^0 \text{ reactants}$, so we use the ΔH_f^0 values tabulated in Appendix K.

Solution

We can first list the ΔH_f^0 values we obtain from Appendix K:

	$\text{SiH}_4(\text{g})$	$\text{O}_2(\text{g})$	$\text{SiO}_2(\text{s})$	$\text{H}_2\text{O}(\ell)$
$\Delta H_f^0, \text{kJ/mol}$:	34.3	0	-910.9	-285.8

$$\Delta H_{\text{rxn}}^0 = \sum n \Delta H_f^0 \text{ products} - \sum n \Delta H_f^0 \text{ reactants}$$

$$\Delta H_{\text{rxn}}^0 = [\Delta H_f^0 \text{ SiO}_2(\text{s}) + 2 \Delta H_f^0 \text{ H}_2\text{O}(\ell)] - [\Delta H_f^0 \text{ SiH}_4(\text{g}) + 2 \Delta H_f^0 \text{ O}_2(\text{g})]$$

$$\Delta H_{\text{rxn}}^0 = \left[\frac{1 \text{ mol SiO}_2(\text{s})}{\text{mol rxn}} \times \frac{-910.9 \text{ kJ}}{\text{mol SiO}_2(\text{s})} + \frac{2 \text{ mol H}_2\text{O}(\ell)}{\text{mol rxn}} \times \frac{-285.8 \text{ kJ}}{\text{mol H}_2\text{O}(\ell)} \right] - \left[\frac{1 \text{ mol SiH}_4(\text{g})}{\text{mol rxn}} \times \frac{+34.3 \text{ kJ}}{\text{mol SiH}_4(\text{g})} + \frac{2 \text{ mol O}_2(\text{g})}{\text{mol rxn}} \times \frac{0 \text{ kJ}}{\text{mol O}_2(\text{g})} \right]$$

$$\Delta H_{\text{rxn}}^0 = -1516.8 \text{ kJ/mol rxn}$$

You should now work Exercise 38.

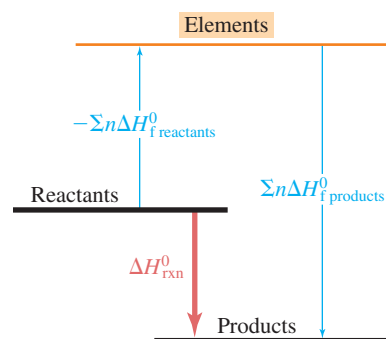


Figure 15-4 A schematic representation of Hess's Law. The red arrow represents the *direct* path from reactants to products. The series of blue arrows is a path (hypothetical) in which reactants are converted to elements, and they in turn are converted to products—all in their standard states.

► $\text{O}_2(\text{g})$ is an element in its standard state, so its ΔH_f^0 is zero.

Each term in the sums on the right-hand side of the solution in Example 15-9 has the units

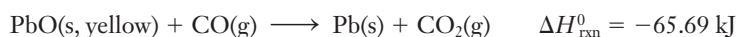
$$\frac{\text{mol substance}}{\text{mol rxn}} \times \frac{\text{kJ}}{\text{mol substance}} \quad \text{or} \quad \frac{\text{kJ}}{\text{mol rxn}}$$

For brevity, we shall omit units in the intermediate steps of calculations of this type, and just assign the proper units to the answer. Be sure that you understand how these units arise.

Suppose we measure ΔH_{rxn}^0 at 298 K and know all but one of the ΔH_f^0 values for reactants and products. We can then calculate the unknown ΔH_f^0 value.

EXAMPLE 15-10 Using ΔH_f^0 Values: Hess's Law

Use the following information to determine ΔH_f^0 for $\text{PbO}(\text{s}, \text{yellow})$.



$$\Delta H_f^0 \text{ for CO}_2(\text{g}) = -393.5 \text{ kJ/mol} \quad \text{and} \quad \Delta H_f^0 \text{ for CO}(\text{g}) = -110.5 \text{ kJ/mol}$$

► We will consult Appendix K to check the answer only after working the problem.

Plan

We again use Hess's Law in the form $\Delta H_{\text{rxn}}^0 = \sum n \Delta H_{\text{f}}^0 \text{ products} - \sum n \Delta H_{\text{f}}^0 \text{ reactants}$. The standard state of lead is Pb(s), so $\Delta H_{\text{f}}^0 \text{ Pb(s)} = 0 \text{ kJ/mol}$. Now we are given ΔH_{rxn}^0 and the ΔH_{f}^0 values for all substances *except* PbO(s, yellow). We can solve for this unknown.

Solution

We list the known ΔH_{f}^0 values:

	PbO(s, yellow)	CO(g)	Pb(s)	CO ₂ (g)
$\Delta H_{\text{f}}^0, \text{ kJ/mol}$:	$\Delta H_{\text{f}}^0 \text{ PbO(s, yellow)}$	-110.5	0	-393.5

$$\Delta H_{\text{rxn}}^0 = \sum n \Delta H_{\text{f}}^0 \text{ products} - \sum n \Delta H_{\text{f}}^0 \text{ reactants}$$

$$\Delta H_{\text{rxn}}^0 = \Delta H_{\text{f}}^0 \text{ Pb(s)} + \Delta H_{\text{f}}^0 \text{ CO}_2(\text{g}) - [\Delta H_{\text{f}}^0 \text{ PbO(s, yellow)} + \Delta H_{\text{f}}^0 \text{ CO(g)}]$$

Substituting values stated in the problem gives

$$-65.69 = 0 + (-393.5) - [\Delta H_{\text{f}}^0 \text{ PbO(s, yellow)} + (-110.5)]$$

Rearranging to solve for, $\Delta H_{\text{f}}^0 \text{ PbO(s, yellow)}$, we have

$$\Delta H_{\text{f}}^0 \text{ PbO(s, yellow)} = 65.69 - 393.5 + 110.5 = -217.3 \text{ kJ/mol of PbO}$$

You should now work Exercise 44.

Problem-Solving Tip Remember the Values of ΔH_{f}^0 for Elements

In Example 15-10, we were not given the value of ΔH_{f}^0 for Pb(s). We should know without reference to tables that ΔH_{f}^0 for an *element* in its most stable form is exactly 0 kJ/mol, so ΔH_{f}^0 for Pb(s) = 0 kJ/mol. But the element *must* be in its most stable form. Thus, ΔH_{f}^0 for O₂(g) is zero, because ordinary oxygen is gaseous and diatomic. We would *not* assume that ΔH_{f}^0 would be zero for oxygen atoms, O(g), or for ozone, O₃(g). Similarly, ΔH_{f}^0 is zero for Cl₂(g) and for Br₂(ℓ), but not for Br₂(g). Recall that bromine is one of the few elements that is liquid at room temperature and 1 atm pressure.

15-9 Bond Energies

Chemical reactions involve the breaking and making of chemical bonds. Energy is always required to break a chemical bond (see Section 7-4). Often this energy is supplied in the form of heat.

► For all practical purposes, the bond energy is the same as bond enthalpy. Tabulated values of average bond energies are actually average bond enthalpies. We use the term "bond energy" rather than "bond enthalpy" because it is common practice to do so.

► We have discussed these changes in terms of absorption or release of heat. Another way of breaking bonds is by absorption of light energy (see Chapter 4). Bond energies can be determined from the energies of the photons that cause bond dissociation.

The **bond energy (B.E.)** is the amount of energy necessary to break *one mole* of bonds in a gaseous covalent substance to form products in the gaseous state at constant temperature and pressure.

The greater the bond energy, the more stable (stronger) the bond is, and the harder it is to break. Thus bond energy is a measure of bond strengths.

Consider the following reaction.



The bond energy of the hydrogen-hydrogen bond is 436 kJ/mol of bonds. In other words, 436 kJ of energy must be absorbed for every mole of H—H bonds that are broken. This endothermic reaction (ΔH_{rxn}^0 is positive) can be written

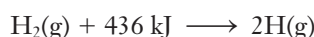


Table 15-2 Some Average Single Bond Energies (kJ/mol of bonds)

H	C	N	O	F	Si	P	S	Cl	Br	I	
436	413	391	463	565	318	322	347	432	366	299	H
	346	305	358	485			272	339	285	213	C
		163	201	283				192			N
			146	190	452	335		218	201	201	O
				155	565	490	284	253	249	278	F
					222		293	381	310	234	Si
						201		326		184	P
							226	255			S
								242	216	208	Cl
									193	175	Br
										151	I

Table 15-3 Comparison of Some Average Single and Multiple Bond Energies (kJ/mol of bonds)

Single Bonds		Double Bonds		Triple Bonds	
C—C	346	C=C	602	C≡C	835
N—N	163	N=N	418	N≡N	945
O—O	146	O=O	498		
C—N	305	C=N	615	C≡N	887
C—O	358	C=O	732*	C≡O	1072

*Except in CO₂, where it is 799 kJ/mol.

Some average bond energies are listed in Tables 15-2 and 15-3. We see from Table 15-3 that for any combination of elements, a triple bond is stronger than a double bond, which in turn is stronger than a single bond. Bond energies for double and triple bonds are *not* simply two or three times those for the corresponding single bonds. A single bond is a σ bond, whereas double and triple bonds involve a combination of σ and π bonding. The bond energy measures the effectiveness of orbital overlap, and we should not expect the strength of a π bond to be the same as that of a σ bond between the same two atoms because π bonds have poorer orbital overlap than σ bonds.

We should keep in mind that each of the values listed is the average bond energy from a variety of compounds. The *average C—H bond energy* is 413 kJ/mol of bonds. Average C—H bond energies differ slightly from compound to compound, as in CH₄, CH₃Cl, CH₃NO₂, and so on. Nevertheless, they are sufficiently constant to be useful in estimating thermodynamic data that are not readily available by another approach. Values of ΔH_{rxn}^0 estimated in this way are not as reliable as those obtained from ΔH_f^0 values for the substances involved in the reaction.

A special case of Hess's Law involves the use of bond energies to *estimate* heats of reaction. Consider the enthalpy diagrams in Figure 15-5. In general terms, ΔH_{rxn}^0 is related to the bond energies of the reactants and products in *gas phase reactions* by the following version of Hess's Law.

$$\Delta H_{\text{rxn}}^0 = \sum \text{B.E.}_{\text{reactants}} - \sum \text{B.E.}_{\text{products}} \quad \text{for gas phase reactions only}$$

The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules *minus* the amount of energy required to break all the bonds in product molecules. Stated in another way, the amount of energy released when a bond is

STOP & THINK

Remember that this equation involves bond energies of *reactants* minus bond energies of *products*. This is opposite Hess's Law, where it is the sum of the products minus the sum of the reactants.

Unless otherwise noted, all content on this page is © Cengage Learning.

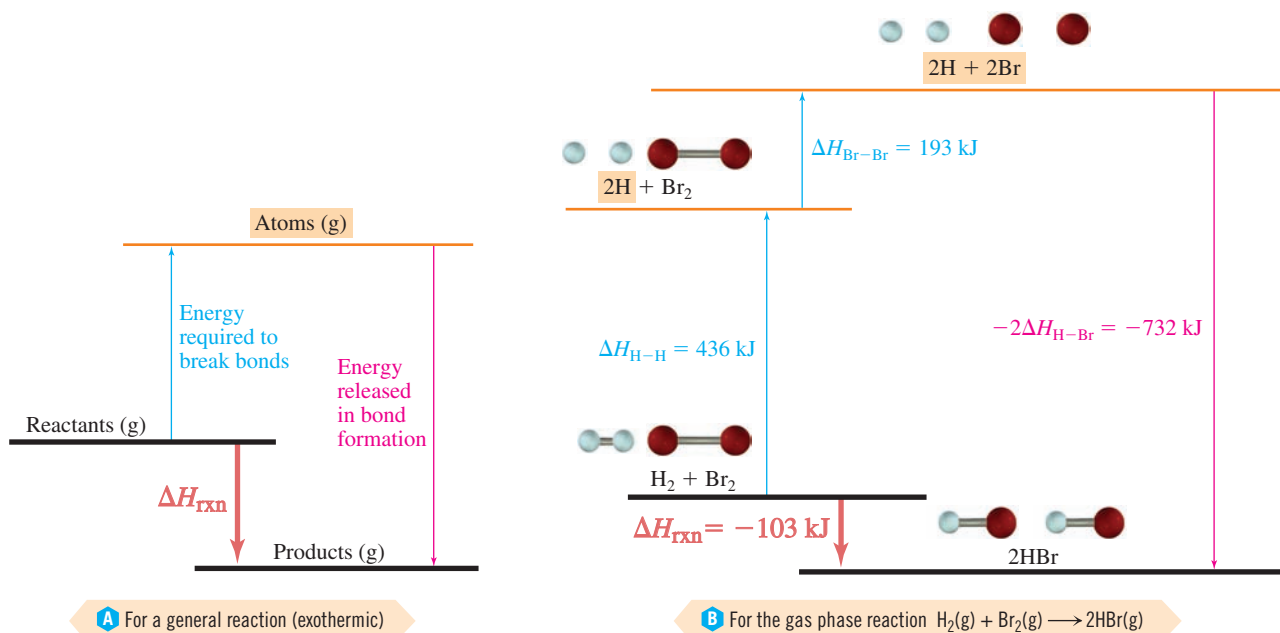


Figure 15-5 A schematic representation of the relationship between bond energies and ΔH_{rxn} for gas phase reactions. As usual for such diagrams, the value shown for each change refers to the number of moles of substances or bonds indicated in the diagram.

► Very few real reactions occur by breaking and forming *all* bonds. But because bond energy is a state function, we can assume *any* pathway between reactants and products and get the same result.

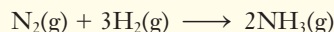
formed is equal to the amount absorbed when the same bond is broken. The heat of reaction for a gas phase reaction can be described as the amount of energy released in forming all the bonds in the products minus the amount of energy released in forming all the bonds in the reactants (see Figure 15-5). This heat of reaction can be estimated using the average bond energies in Tables 15-2 and 15-3.

The definition of bond energies is limited to the bond-breaking process *only* and does not include any provision for changes of state. Thus, it is valid only for substances in the gaseous state. The calculations of this section therefore apply *only* when all substances in the reaction are gases. If liquids or solids were involved, then additional information such as heats of vaporization and fusion would be needed to account for phase changes.

EXAMPLE 15-11 Bond Energies



Use the bond energies listed in Table 15-2 to estimate the heat of reaction at 298 K for the following reaction.



Plan

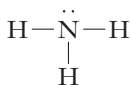
Each NH_3 molecule contains three $\text{N}-\text{H}$ bonds, so two moles of NH_3 contain six moles of $\text{N}-\text{H}$ bonds. Three moles of H_2 contain a total of three moles of $\text{H}-\text{H}$ bonds, and one mole of N_2 contains one mole of $\text{N}\equiv\text{N}$ bonds. From this we can estimate the heat of reaction.

Solution

Using the bond energy form of Hess's Law,

$$\begin{aligned}\Delta H_{\text{rxn}}^0 &= [\Delta H_{\text{N}\equiv\text{N}} + 3\Delta H_{\text{H}-\text{H}}] - [6\Delta H_{\text{N}-\text{H}}] \\ &= 945 + 3(436) - 6(391) = -93 \text{ kJ/mol rxn}\end{aligned}$$

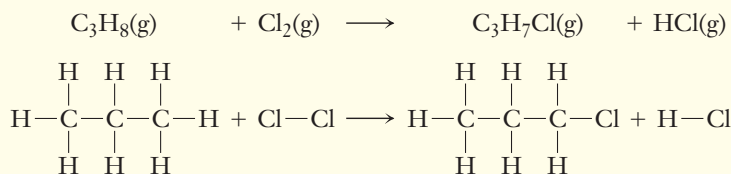
You should now work Exercise 48.



► For each term in the sum, the units are $\frac{\text{mol bonds}}{\text{mol rxn}} \times \frac{\text{kJ}}{\text{mol bonds}}$

EXAMPLE 15-12 Bond Energies

Use the bond energies listed in Table 15-2 to estimate the heat of reaction at 298 K for the following reaction.

**Plan**

Two moles of C—C bonds and seven moles of C—H bonds are the same before and after reaction, so we do not need to include them in the bond energy calculation. The only reactant bonds that are broken are one mole of C—H bonds and one mole of Cl—Cl bonds. On the product side, the only new bonds formed are one mole of C—Cl bonds and one mole of H—Cl bonds. We need to take into account only the bonds that are different on the two sides of the equation. As before, we add and subtract the appropriate bond energies, using values from Table 15-2.

Solution

$$\begin{aligned} \Delta H_{\text{rxn}}^0 &= [\Delta H_{\text{C-H}} + \Delta H_{\text{Cl-Cl}}] - [\Delta H_{\text{C-Cl}} + \Delta H_{\text{H-Cl}}] \\ &= [413 + 242] - [339 + 432] = -116 \text{ kJ/mol rxn} \end{aligned}$$

You should now work Exercises 50 and 52.

STOP & THINK

We would get the same value for ΔH_{rxn}^0 if we used the full bond energy form of Hess's Law and assumed that *all* bonds in reactants were broken and then *all* bonds in products were formed. In such a calculation the bond energies for the unchanged bonds would cancel. Why? Try it!

15-10 Changes in Internal Energy, ΔE

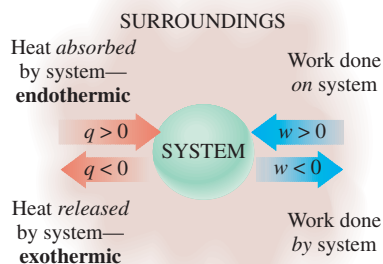
The **internal energy**, E , of a specific amount of a substance represents all the energy contained within the substance. It includes such forms as kinetic energies of the molecules; energies of attraction and repulsion among subatomic particles, atoms, ions, or molecules; and other forms of energy. The internal energy of a collection of molecules is a state function. The difference between the internal energy of the products and the internal energy of the reactants of a chemical reaction or physical change, ΔE , is given by the equation

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{products}} - E_{\text{reactants}} = q + w$$

The terms q and w represent heat and work, respectively. These are two ways in which energy can flow into or out of a system. **Work** involves a change of energy in which a body is moved through a distance, d , against some force, f ; that is, $w = fd$.

$$\Delta E = (\text{amount of heat absorbed by system}) + (\text{amount of work done on system})$$

► Internal energy is a state function, so it is represented by a capital letter.



Sign conventions for q and w .

Unless otherwise noted, all content on this page is © Cengage Learning.



A Some powdered dry ice (solid CO_2) is placed into a flexible bag, which is then sealed.



Charles D. Winters

B As the dry ice absorbs heat from the surroundings, some solid CO_2 sublimates to form gaseous CO_2 . The larger volume of the gas causes the bag to expand. The expanding gas does the work of raising a book that has been placed on the bag. Work would be done by the expansion, even if the book were not present, as the bag pushes against the surrounding atmosphere. The heat absorbed by such a process at constant pressure, q_p , is equal to ΔH for the process.

Figure 15-6 A system that absorbs heat and does work.

$$\frac{F}{d^2} \times d^3 = Fd = w$$

$$\begin{array}{c} \uparrow \quad \uparrow \\ P \quad V \end{array}$$

► At 25° the change in internal energy for the combustion of methane is -887 kJ/mol CH_4 . The change in heat content is -890 kJ/mol CH_4 (see Section 15-1). The small difference is due to work done on the system as it is compressed by the atmosphere.

The following conventions apply to the signs of q and w .

q is positive:	Heat is <i>absorbed</i> by the system from the surroundings (endothermic).
q is negative:	Heat is <i>released</i> by the system to the surroundings (exothermic).
w is positive:	Work is done <i>on</i> the system by the surroundings.
w is negative:	Work is done <i>by</i> the system on the surroundings.

Whenever a given amount of energy is added to or removed from a system, either as heat or as work, the energy of the system changes by that same amount. The equation $\Delta E = q + w$ is another way of expressing the First Law of Thermodynamics (see Section 15-1).

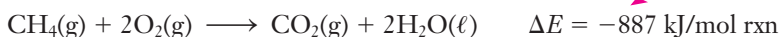
The only type of work involved in most chemical and physical changes is pressure-volume work. From dimensional analysis we can see that the product of pressure and volume is work. Pressure is the force exerted per unit area, where area is distance squared, d^2 ; volume is distance cubed, d^3 . Thus, the product of pressure and volume is force times distance, which is work. An example of a physical change (a phase change) in which the system expands and thus does work as it absorbs heat is shown in Figure 15-6. Even if the book had not been present, the expanding system pushing against the atmosphere would have done work for the expansion.

When energy is released by a reacting system, ΔE is negative; energy can be written as a product in the equation for the reaction. When the system absorbs energy from the surroundings, ΔE is positive; energy can be written as a reactant in the equation.

For example, the complete combustion of CH_4 at constant volume at 25°C *releases* energy.

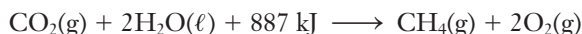


We can write the *change in energy* that accompanies this reaction as

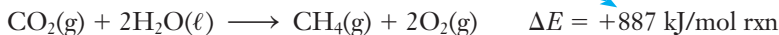


As discussed in Section 15-2, the negative sign indicates a *decrease* in energy of the system, or a *release* of energy by the system.

The reverse of this reaction *absorbs* energy. It can be written as



or



If the latter reaction could be forced to occur, the system would have to absorb 887 kJ of energy per mole of reaction from its surroundings.

When a gas is produced against constant external pressure, such as in an open vessel at atmospheric pressure, the gas does work as it expands against the pressure of the atmosphere. If no heat is absorbed during the expansion, the result is a decrease in the internal energy of the system. On the other hand, when a gas is consumed in a process, the atmosphere does work on the reacting system.

Let us illustrate the latter case. Consider the complete reaction of a 2:1 mole ratio of H_2 and O_2 to produce steam at some constant temperature above 100°C and at one atmosphere pressure (Figure 15-7).



Assume that the constant-temperature bath surrounding the reaction vessel completely absorbs all the evolved heat so that the temperature of the gases does not change. The volume of the system decreases by one third (3 mol gaseous reactants $\rightarrow$ 2 mol gaseous products). The surroundings exert a constant pressure of one atmosphere and do work on the system by compressing it. The internal energy of the system increases by an amount equal to the amount of work done on it.

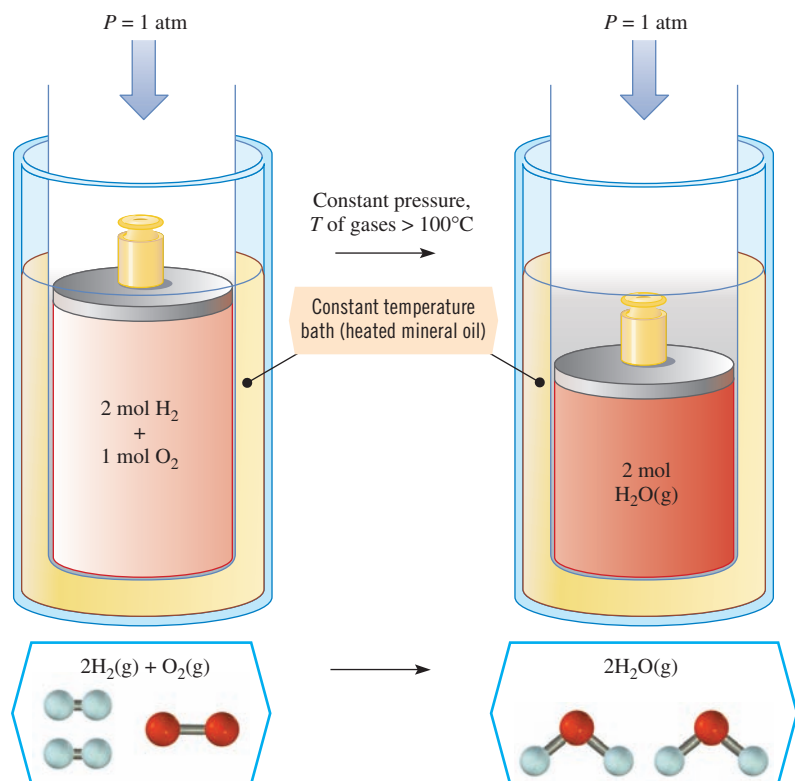


Figure 15-7 An illustration of the one-third decrease in volume that accompanies the reaction of H_2 with O_2 at constant temperature. The temperature is above 100°C .

The work done on or by a system depends on the *external* pressure and the volume. When the external pressure is constant during a change, the amount of work done is equal to this pressure times the change in volume. The work done *on* a system equals $-P \Delta V$ or $-P(V_2 - V_1)$.

► V_2 is the final volume, and V_1 is the initial volume.

Compression (volume decreases)	Expansion (volume increases)
Work is done <i>by</i> the surroundings <i>on</i> the system, so the sign of w is positive V_2 is less than V_1, so $\Delta V = (V_2 - V_1)$ is negative $w = -P \Delta V$ is positive $(-) \times (+) \times (-) = +$ Can be due to a <i>decrease</i> in number of moles of gas (Δn negative)	Work is done <i>by</i> the system <i>on</i> the surroundings, so the sign of w is negative V_2 is greater than V_1, so $\Delta V = (V_2 - V_1)$ is positive $w = -P \Delta V$ is negative $(-) \times (+) \times (+) = -$ Can be due to an <i>increase</i> in number of moles of gas (Δn positive)

We substitute $-P \Delta V$ for w in the equation $\Delta E = q + w$ to obtain

$$\Delta E = q - P \Delta V$$

In constant-volume reactions, no $P \Delta V$ work is done. Volume does not change, so nothing “moves through a distance,” and $d = 0$ and $f d = 0$. The change in internal energy of the system is just the amount of heat absorbed or released at constant volume, q_v .

$$\Delta E = q_v$$

Figure 15-8 shows the same phase change process as in Figure 15-6, but at constant volume condition, so no work is done.

Solids and liquids do not expand or contract significantly when the pressure changes ($\Delta V \approx 0$). In reactions in which equal numbers of moles of gases are produced and con-

► Do not make the error of setting work equal to $V \Delta P$.

► A subscript v indicates a constant-volume process; a subscript p indicates a constant-pressure process.



Figure 15-8 A system that absorbs heat at constant volume. Some dry ice [CO₂(s)] is placed into a rigid flask, which is then sealed. As the dry ice absorbs heat from the surroundings, some CO₂(s) sublimates to form CO₂(g). In contrast to the case in Figure 15-6, this system cannot expand ($\Delta V = 0$), so no work is done, and the pressure in the flask increases. Thus, the heat absorbed at constant volume, q_v , is equal to ΔE for the process.

► Δn refers to the balanced equation.

sumed at constant temperature and pressure, essentially no work is done. By the ideal gas equation, $P \Delta V = (\Delta n)RT$ and $\Delta n = 0$, where Δn equals the number of moles of gaseous products minus the number of moles of gaseous reactants. Thus, the work term w has a significant value at constant pressure only when there are different numbers of moles of gaseous products and reactants so that the volume of the system changes.

EXAMPLE 15-13 Predicting the Sign of Work

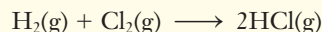
For each of the following chemical reactions carried out at constant temperature and constant pressure, predict the sign of w and tell whether work is done *on* or *by* the system. Consider the reaction mixture to be the system.

- (a) Ammonium nitrate, commonly used as a fertilizer, decomposes explosively.

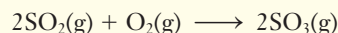


This reaction was responsible for an explosion in 1947 that destroyed nearly the entire port of Texas City, Texas, and killed 576 people.

- (b) Hydrogen and chlorine combine to form hydrogen chloride gas.



- (c) Sulfur dioxide is oxidized to sulfur trioxide, one step in the production of sulfuric acid.



Plan

For a process at constant pressure, $w = -P \Delta V = -(\Delta n)RT$. For each reaction, we evaluate Δn , the change in the number of moles of *gaseous* substances in the reaction.

$$\Delta n = (\text{no. of moles of gaseous products}) - (\text{no. of moles of gaseous reactants})$$

Because both R and T (on the Kelvin scale) are positive quantities, the sign of w is opposite from that of Δn ; it tells us whether the work is done *on* ($w = +$) or *by* ($w = -$) the system.



The decomposition of NH_4NO_3 produces large amounts of gas, which expands rapidly as the very fast reaction occurs. This explosive reaction was the main cause of the destruction of the Federal Building in Oklahoma City in 1995.

Solution

$$\begin{aligned} \text{(a)} \quad \Delta n &= [2 \text{ mol N}_2(\text{g}) + 4 \text{ mol H}_2\text{O}(\text{g}) + 1 \text{ mol O}_2(\text{g})] - 0 \text{ mol} \\ &= 7 \text{ mol} - 0 \text{ mol} = +7 \text{ mol} \end{aligned}$$

Δn is positive, so w is negative. This tells us that work is done *by* the system. The large amount of gas formed by the reaction pushes against the surroundings (as happened with devastating effect in the Texas City disaster).

$$\begin{aligned} \text{(b)} \quad \Delta n &= [2 \text{ mol HCl}(\text{g})] - [1 \text{ mol H}_2(\text{g}) + 1 \text{ mol Cl}_2(\text{g})] \\ &= 2 \text{ mol} - 2 \text{ mol} = 0 \text{ mol} \end{aligned}$$

Thus, $w = 0$, and no work is done as the reaction proceeds. We can see from the balanced equation that for every two moles (total) of gas that react, two moles of gas are formed, so the volume neither expands nor contracts as the reaction occurs.

► Here there are no gaseous reactants.

$$\begin{aligned} \text{(c) } \Delta n &= [2 \text{ mol SO}_3(\text{g})] - [2 \text{ mol SO}_2(\text{g}) + 1 \text{ mol O}_2(\text{g})] \\ &= 2 \text{ mol} - 3 \text{ mol} = -1 \text{ mol} \end{aligned}$$

Δn is negative, so w is positive. This tells us that work is done *on* the system as the reaction proceeds. The surroundings push against the diminishing volume of gas.

You should now work Exercises 77 and 78.

STOP & THINK

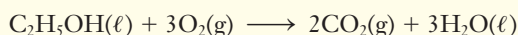
When the number of moles of gas *increases*, work is done *by* the system, so w is *negative*. When the number of moles of gas *decreases*, work is done *on* the system, so w is *positive*.

A **bomb calorimeter** is a device that measures the amount of heat evolved or absorbed by a reaction occurring at constant volume (Figure 15-9). A strong steel vessel (the bomb) is immersed in a large volume of water. As heat is produced or absorbed by a reaction inside the steel vessel, the heat is transferred to or from the large volume of water. Thus, only rather small temperature changes occur. For all practical purposes, the energy changes associated with the reactions are measured at constant volume and constant temperature. No work is done when a reaction is carried out in a bomb calorimeter, even if gases are involved, because $\Delta V = 0$. Therefore,

$$\Delta E = q_v \quad (\text{constant volume})$$

EXAMPLE 15-14 Bomb Calorimeter

A 1.000-gram sample of ethanol, $\text{C}_2\text{H}_5\text{OH}$, was burned in a bomb calorimeter whose heat capacity had been determined to be $2.71 \text{ kJ}/^\circ\text{C}$. The temperature of 3000 grams of water rose from 24.284°C to 26.225°C . Determine ΔE for the reaction in joules per gram of ethanol, and then in kilojoules per mole of ethanol. The specific heat of water is $4.184 \text{ J/g} \cdot ^\circ\text{C}$. The combustion reaction is



Plan

The amount of heat given off by the system (in the sealed compartment) raises the temperature of the calorimeter and its water. The amount of heat absorbed by the water can be calculated using the specific heat of water; similarly, we use the heat capacity of the calorimeter to find the amount of heat absorbed by the calorimeter. The sum of these two amounts of heat is the total amount of heat released by the combustion of 1.000 gram of ethanol. We must then scale that result to correspond to one mole of ethanol.

Solution

The increase in temperature is

$$\Delta T = 26.225^\circ\text{C} - 24.284^\circ\text{C} = 1.941^\circ\text{C} \text{ rise}$$

The amount of heat responsible for this increase in temperature of 3000 grams of water is

$$\text{heat to warm water} = 1.941^\circ\text{C} \times \frac{4.184 \text{ J}}{\text{g} \cdot ^\circ\text{C}} \times 3000 \text{ g} = 2.436 \times 10^4 \text{ J} = 24.36 \text{ kJ}$$

The amount of heat responsible for the warming of the calorimeter is

$$\text{heat to warm calorimeter} = 1.941^\circ\text{C} \times \frac{2.71 \text{ kJ}}{^\circ\text{C}} = 5.26 \text{ kJ}$$

The total amount of heat absorbed by the calorimeter *and* by the water is

$$\text{total amount of heat} = 24.36 \text{ kJ} + 5.26 \text{ kJ} = 29.62 \text{ kJ}$$

Combustion of one gram of $\text{C}_2\text{H}_5\text{OH}$ liberates 29.62 kJ of energy in the form of heat, that is

$$\Delta E = q_v = -29.62 \text{ kJ/g ethanol}$$

► The “calorie content” of a food can be determined by burning it in excess oxygen inside a bomb calorimeter and determining the heat released. 1 “nutritional Calorie” = 1 kcal = 4.184 kJ.

► Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, is often used to determine the heat capacity of a calorimeter. It is a solid that can be compressed into pellets. Its heat of combustion is accurately known: 3227 kJ/mol benzoic acid, or 26.46 kJ/g benzoic acid. Another way to measure the heat capacity of a calorimeter is to add a known amount of heat electrically.



A disassembled bomb calorimeter

Charles D. Winters

Unless otherwise noted, all content on this page is © Cengage Learning.

The negative sign indicates that energy is released by the system to the surroundings. Now we may evaluate ΔE in kJ/mol of ethanol by converting grams of $\text{C}_2\text{H}_5\text{OH}$ to moles.

$$\frac{? \text{ kJ}}{\text{mol ethanol}} = \frac{-29.62 \text{ kJ}}{\text{g}} \times \frac{46.07 \text{ g C}_2\text{H}_5\text{OH}}{1 \text{ mol C}_2\text{H}_5\text{OH}} = -1365 \text{ kJ/mol ethanol}$$

$$\Delta E = -1365 \text{ kJ/mol ethanol}$$

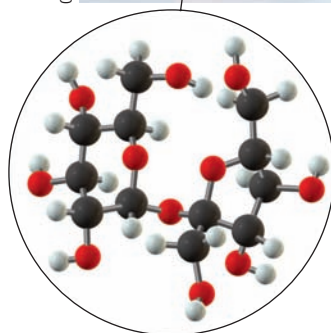
This calculation shows that for the combustion of ethanol at constant temperature and constant volume, the change in internal energy is $-1365 \text{ kJ/mol ethanol}$.

You should now work Exercises 66 and 67.

The balanced chemical equation involves one mole of ethanol, so we can write the unit factor $\frac{1 \text{ mol ethanol}}{1 \text{ mol rxn}}$. Then we express the result of Example 15-14 as

$$\Delta E = \frac{-1365 \text{ kJ}}{\text{mol ethanol}} \times \frac{1 \text{ mol ethanol}}{1 \text{ mol rxn}} = -1365 \text{ kJ/mol rxn}$$

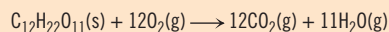
A This small piece of candy is mostly sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, a sugar.



Oxidation of sugar.



B When the piece of candy is heated together with potassium chlorate, KClO_3 (a good oxidizing agent), a highly product-favored reaction occurs.



If that amount of sucrose is completely metabolized to carbon dioxide and water vapor in your body, the same amount of energy is released, though more slowly.

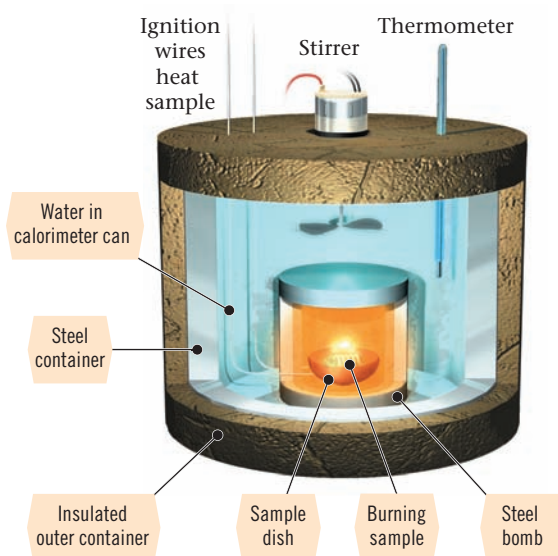


Figure 15-9 A bomb calorimeter measures q_v , the amount of heat given off or absorbed by a reaction occurring at constant volume. The amount of energy introduced via the ignition wires is measured and taken into account.

15-11 Relationship Between ΔH and ΔE

The fundamental definition of enthalpy, H , is

$$H = E + PV$$

For a process at constant temperature and pressure,

$$\Delta H = \Delta E + P \Delta V \quad (\text{constant } T \text{ and } P)$$

From Section 15-10, we know that $\Delta E = q + w$, so

$$\Delta H = q + w + P \Delta V \quad (\text{constant } T \text{ and } P)$$

At constant pressure, $w = -P \Delta V$, so

$$\Delta H = q + (-P \Delta V) + P \Delta V$$

$$\Delta H = q_p \quad (\text{constant } T \text{ and } P)$$

The difference between ΔE and ΔH is the amount of expansion work ($P \Delta V$ work) that the system can do. Unless there is a change in the number of moles of gas present, this difference is extremely small and can usually be neglected. For an ideal gas, $PV = nRT$. At constant temperature and constant pressure, $P \Delta V = (\Delta n)RT$, a work term. Substituting gives

$$\Delta H = \Delta E + (\Delta n)RT \quad \text{or} \quad \Delta E = \Delta H - (\Delta n)RT \quad (\text{constant } T \text{ and } P)$$

Problem-Solving Tip Two Equations Relate ΔH and ΔE —Which One Should Be Used?

The relationship $\Delta H = \Delta E + P \Delta V$ is valid for *any* process that takes place at constant temperature and pressure. It is very useful for physical changes that involve volume changes, such as expansion or compression of a gas.

When a chemical reaction occurring at constant T and P results in a change in the number of moles of gas, it is more convenient to use the relationship in the form $\Delta H = \Delta E + (\Delta n)RT$. You should always remember that Δn refers to the change in the number of moles of *gas in the balanced chemical equation*.

STOP & THINK

As usual, Δn refers to the number of moles of *gaseous products* minus the number of moles of *gaseous reactants* in the *balanced chemical equation*.

In Example 15-14 we found that the change in internal energy, ΔE , for the combustion of ethanol is -1365 kJ/mol ethanol at 298 K . Combustion of one mole of ethanol at 298 K and constant pressure releases 1367 kJ of heat. Therefore (see Section 15-5)

$$\Delta H = -1367 \frac{\text{kJ}}{\text{mol ethanol}}$$

The difference between ΔH and ΔE is due to the work term, $-P \Delta V$ or $-(\Delta n)RT$. In this balanced equation there are fewer moles of gaseous products than of gaseous reactants: $\Delta n = 2 - 3 = -1$.



Thus, the atmosphere does work on the system (compresses it). Let us find the work done on the system per mole of reaction.

$$\begin{aligned} w &= -P \Delta V = -(\Delta n)RT \\ &= -(-1 \text{ mol}) \left(\frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \right) (298 \text{ K}) = +2.48 \times 10^3 \text{ J} \\ w &= +2.48 \text{ kJ} \quad \text{or} \quad (\Delta n)RT = -2.48 \text{ kJ} \end{aligned}$$

We can now calculate ΔE for the reaction from ΔH and $(\Delta n)RT$ values.

$$\Delta E = \Delta H - (\Delta n)RT = [-1367 - (-2.48)] = -1365 \text{ kJ/mol rxn}$$

This value agrees with the result that we obtained in Example 15-14. The size of the work term ($+2.48 \text{ kJ}$) is very small compared with ΔH (-1367 kJ/mol rxn). This is true for many reactions. Of course, if $\Delta n = 0$, then $\Delta H = \Delta E$, and the same amount of heat would be absorbed or given off by the reaction whether it is carried out at constant pressure or at constant volume.

STOP & THINK

The positive sign for w is consistent with the fact that work is done on the system. The balanced equation involves one mole of ethanol, so this is the amount of work done when one mole of ethanol undergoes combustion.

Spontaneity of Physical and Chemical Changes

Another major concern of thermodynamics is predicting *whether* a particular process can occur under specified conditions to give predominantly products. We may summarize this concern in the question “Which would be more stable at the given conditions—the reactants or the products?” A change for which the collection of products is thermodynamically *more stable* than the collection of reactants under the given conditions is said to be **product-favored**, or **spontaneous**, under those conditions. A change for which the products are thermodynamically *less stable* than the reactants under the given conditions is described as **reactant-favored**, or **nonspontaneous**, under those conditions. Some changes are spontaneous under all conditions; others are nonspontaneous under all conditions. The great majority of changes, however, are spontaneous under some conditions but not under others. We use thermodynamics to predict conditions for which the latter type of reactions can occur to give predominantly products.

The concept of spontaneity has a specific interpretation in thermodynamics. A spontaneous chemical reaction or physical change is one that can happen without any continuing outside influence. Examples are the loss of heat by a hot metal to its cooler surroundings, the rusting of a piece of iron, the expansion of a gas into a larger volume, or the melting of ice at room temperature. Such changes have a tendency to occur without being driven by an external influence. We can think of a spontaneous process as one for which products are favored over reactants *at the specified conditions*. The reverse of each of the spontaneous changes just listed is nonspontaneous at the same conditions, that is, it does not occur naturally. We can, however, cause some *nonspontaneous* changes to occur. For example, forcing an electric current through a block of metal can heat it to a temperature higher than that of its surroundings. We can compress a gas into a smaller volume by pressing on it with a piston. But to cause a process to occur in its *nonspontaneous* direction, we must influence it from outside the system; that is, energy must be added to the system.



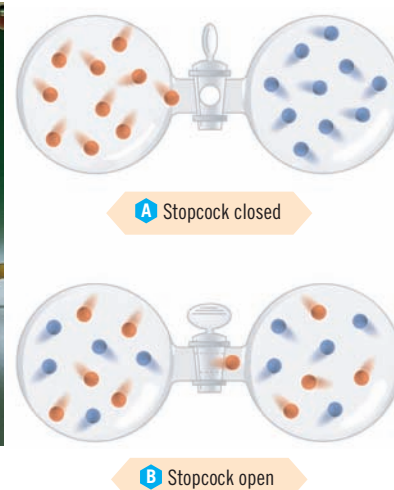
Charles D. Winters

A

A hot piece of metal (a) is placed into cooler water. Heat is transferred *spontaneously* from the hotter metal to the cooler water (b), until the two are at the same temperature (the condition of *thermal equilibrium*).



B



A Stopcock closed

B Stopcock open

Figure 15-10 The diffusion of two gases into one another is spontaneous. (a) A sample of gas in which all molecules of one gas are in one bulb and all molecules of the other gas are in the other bulb. (b) A sample of gas that contains the same number of each kind of molecule as in (a), but with the two kinds randomly mixed in the two bulbs. Sample (b) has greater dispersal of both matter and energy, and is thus more probable.

Although a spontaneous reaction *might* occur rapidly, thermodynamic spontaneity is not related to speed. The fact that a process is spontaneous does not mean that it will occur at an observable rate. It may occur rapidly, at a moderate rate, or very slowly. The rate at which a spontaneous reaction occurs is addressed by kinetics (see Chapter 16).

We now study the factors that influence spontaneity of a physical or chemical change.

15-12 The Two Aspects of Spontaneity

Many product-favored reactions are exothermic. For instance, the combustion (burning) reactions of hydrocarbons such as methane and octane are all exothermic and highly product-favored (spontaneous). The total enthalpy content of the products is lower than that of the reactants. Not all exothermic changes are spontaneous, however, nor are all spontaneous changes exothermic. As an example, consider the freezing of water, which is an exothermic process (heat is released). This process is spontaneous at temperatures below 0°C, but we know it is not spontaneous at temperatures above 0°C. Likewise, we know there are conditions at which the melting of ice, an endothermic process, is spontaneous. Spontaneity is *favored* but not required when heat is released during a chemical reaction or a physical change.

There is another factor that also plays a fundamental role in determining spontaneity. Let's think about two spontaneous processes. Figure 15-10 shows what happens when two gas samples at the same pressure are allowed to mix. The molecules move randomly throughout the two containers to mix the gases (a spontaneous process). We don't expect the more homogeneous sample in Figure 15-10b to spontaneously "unmix" to give the arrangement in Figure 15-10a (a nonspontaneous process).

As a hot metal cools, some of the energy of its vibrating atoms is transferred to the surroundings (a spontaneous process). This warms the surroundings until the two temperatures are equal. We do not expect to observe the reverse process in which energy is transferred from the surroundings to a block of metal, originally at the same temperature, to raise the temperature of the metal (a nonspontaneous process).

In these examples, we see that *energy and matter tend to become dispersed (spread out)*. We shall see that this dispersal is a fundamental driving force that affects the spontaneity of any process.

► Recall that the temperature of a sample is a measure of the average kinetic energy of its particles.

Two factors affect the spontaneity of any physical or chemical change:

1. Spontaneity is *avored* when *heat is released* during the change (exothermic).
2. Spontaneity is *avored* when the change causes an *increase in the dispersal of energy and matter*.

The balance of these two effects is considered in Section 15-16.

15-13 Dispersal of Energy and Matter

Dispersal of Energy

The **dispersal of energy** in a system results in the energy being spread over many particles rather than being concentrated in just a few.

To understand this concept, think about a system consisting of just two molecules, A and B, with a total of two units of energy. Denoting one unit of energy with a^* , we can list the three ways to distribute these two energy units over the two molecules as

A^{**} (Molecule A has two units of energy, B has none.)

A^*B^* (Each molecule has one unit of energy.)

B^{**} (Molecule B has two units of energy, A has none.)

Suppose these two molecules are mixed with two other molecules, C and D, that initially have no energy. When collisions occur, energy can be transferred from one molecule to another. Now the energy can be dispersed among the four molecules in ten different ways:

$A^{**} \quad B^{**} \quad C^{**} \quad D^{**} \quad A^*B^* \quad A^*C^* \quad A^*D^* \quad B^*C^* \quad B^*D^* \quad C^*D^*$

Now there are obviously more ways (ten) the energy can be dispersed than before. In only three of these ways would all of the energy be distributed as before— A^{**} , A^*B^* , and B^{**} . Put another way, there is only a 3/10 probability that the energy will be restricted to the original molecules, A and B. There are seven ways out of ten, or a probability of 7/10, that at least some of the energy has been transferred to C or D.

What would happen if large numbers of molecules were present, as in any real sample? The probability that the energy is dispersed would be huge, and there would be only an infinitesimally small chance that all of the energy would be concentrated in one or a few molecules. This reasoning leads us to an important conclusion.

If energy can be dispersed over a larger number of particles, it will be.

To see what happens if there is more energy to distribute (as at a higher temperature), let's consider another system with four molecules, but with two of the molecules (A and B) initially having three units of energy and the other two (C and D) initially with no energy, as shown in Figure 15-11a. When these molecules are brought together and allowed to exchange energy by colliding, the energy can be distributed in a total of 84 different ways, as shown in Figure 15-11b. For example, one molecule can have all six units of energy and the other three have no energy, as shown in the leftmost drawing of Figure 15-11b; the six-unit molecule could be any one of the four, so there are four ways to achieve this arrangement. Thus, the probability is only 4/84 (or 1/21) that all of the energy of the system is concentrated in one molecule. There are six ways to distribute the energy to arrive at the rightmost drawing (see Figure 15-11c). Some of the other energy distributions can be achieved in many more ways, leading to a much higher probability for their occurrence. This leads to a broader statement of our earlier conclusion.

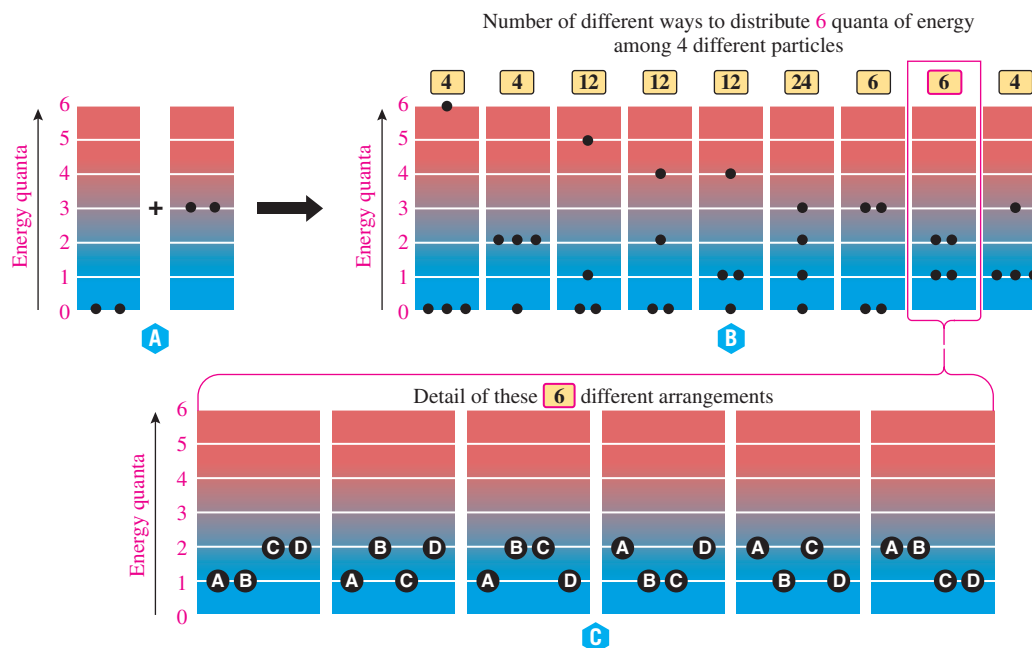


Figure 15-11 Possible ways of distributing six quanta of energy among four molecules. (a) Initially four molecules are separated from each other. Two molecules each have three quanta of energy, and the other two have none. A total of six quanta of energy will be distributed once the molecules interact. (b) Once the molecules begin to interact, there are nine ways to distribute the six available quanta. Each of these arrangements will have multiple ways of distributing the energy among the four molecules. (c) The six different ways to arrange four molecules (A, B, C, and D) such that two molecules have two quanta of energy and the other two have one quanta of energy.

The greater the number of molecules and the higher the total energy of the system, the less likely the energy will be concentrated in a few molecules. Therefore, the energy will be more dispersed.

This generalization provides the molecular explanation behind the Maxwell-Boltzmann distribution of molecular speeds (kinetic energies) that was discussed in Section 12-13 (see Figure 12-9) and in relation to evaporation and vapor pressures of liquids in Sections 13-6 and 13-7.

Dispersal of Matter

Let us apply the idea of dispersal to the arrangements of matter and its molecules. Our experience tells us that a gas originally confined in a bulb (Figure 15-12a) will expand freely into a vacuum (see Figure 15-12b). We don't expect the gas then to concentrate spontaneously into only one bulb. We can consider this expansion from the molecular point of view.

Suppose there are four molecules of gas in the two-part container of Figure 15-13. The probability that a particular molecule is on the left at any given time is $\frac{1}{2}$. A second specific molecule has its own probability of $\frac{1}{2}$ of being on the left, so the probability that *both* of these are on the left at the same time is $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$. There are 16 ways that the molecules can be arranged in this container. But in only one of these arrangements are all four molecules in the left-hand portion of the container. The probability of that "concentrated" arrangement is

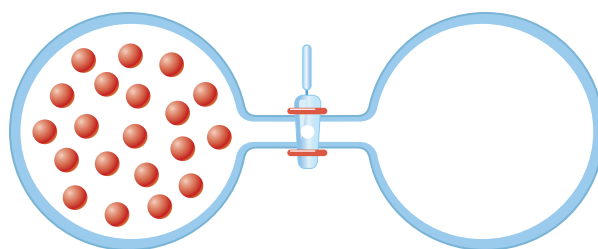
$$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$$

We see that there is only a small likelihood that this gas would spontaneously concentrate into the left side of the container.

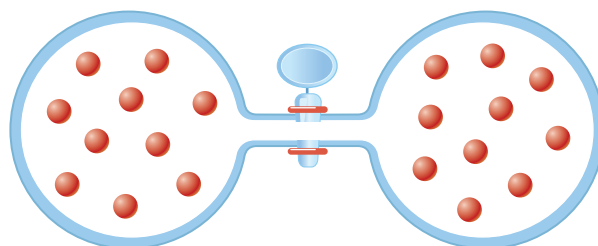
Similar reasoning shows that the probability of one mole, or 6.0×10^{23} molecules, spontaneously concentrating into the left-hand bulb of Figure 15-12 would be

$$\frac{1}{2} \times \frac{1}{2} \times \dots \times \frac{1}{2} = \left(\frac{1}{2}\right)^{6.0 \times 10^{23}} = \frac{1}{2^{6.0 \times 10^{23}}}$$

Without writing the number in the denominator explicitly, we can mention that it is larger than the number of molecules in the entire universe! Thus there is virtually no chance that



A The stopcock is closed, keeping all of the gas in the left bulb; the right bulb is empty (a vacuum).



B When the stopcock is opened, the gas expands to fill the entire available volume, with half of the gas in each bulb.

Figure 15-12 The expansion of a gas into a vacuum.

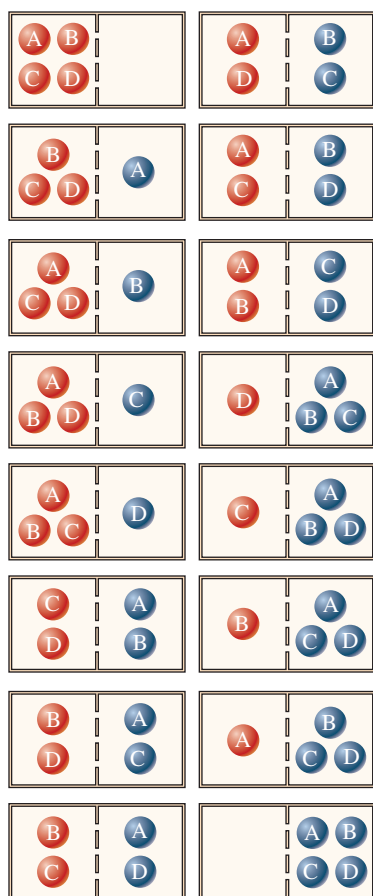


Figure 15-13 The 16 possible ways of arranging four molecules in a two-part container. Only one of these arrangements has all four molecules on the left side, so the probability of that arrangement is $1/16$.

all 6.0×10^{23} molecules in a mole of gas would spontaneously concentrate into half the available volume, leaving no molecules in the other half.

The dispersal of matter, as in the expansion of a gas, also often contributes to energy dispersal. Consider the expansion of a gas into a vacuum, as shown in Figure 15-14. When the gas is allowed to occupy the larger volume in Figure 15-14b, its energy levels become closer together than in the smaller volume of Figure 15-14a. This means that there are even more ways for the expanded gas to disperse its energy to arrive at the same total energy. The concept of dispersal of energy thus also predicts that the gas is far more likely to exist in the expanded state of Figure 15-14b, and we would not expect it to concentrate spontaneously to occupy only one chamber as in Figure 15-14a. Similar reasoning helps us to describe the spontaneous mixing of two gases in Figure 15-10. Each gas can have its energy more dispersed in its own more closely spaced energy levels when expanded into both containers. But in addition, the molecules of one gas can transfer energy to the molecules of the other gas by collision. This results in an even larger number of ways for the total energy of the mixture to be dispersed, leading to a much higher probability that the gases will be mixed (see Figure 15-10b) than unmixed (see Figure 15-10a). Thus the spatial dispersal of matter also results in a greater dispersal of energy.

When a soluble substance dissolves in a liquid, the solute particles become dispersed in the solvent (see Sections 14-1 through 14-4). This allows the particles to transfer energy to one another, giving a larger number of ways of distributing the same total energy than if the substances remained in separate phases. In this case, too, dispersal of the two kinds of matter in one another allows more dispersal of energy. In more general terms, we often describe the dispersal of matter as an increase in **disorder**.

To summarize the conclusions of this section:

The final state of a system can be more probable than its initial state (spontaneous, product-favored) in either or both of two ways:

1. Energy can be dispersed over a greater number and variety of molecules.
2. The particles of the system can be more dispersed (more disordered).

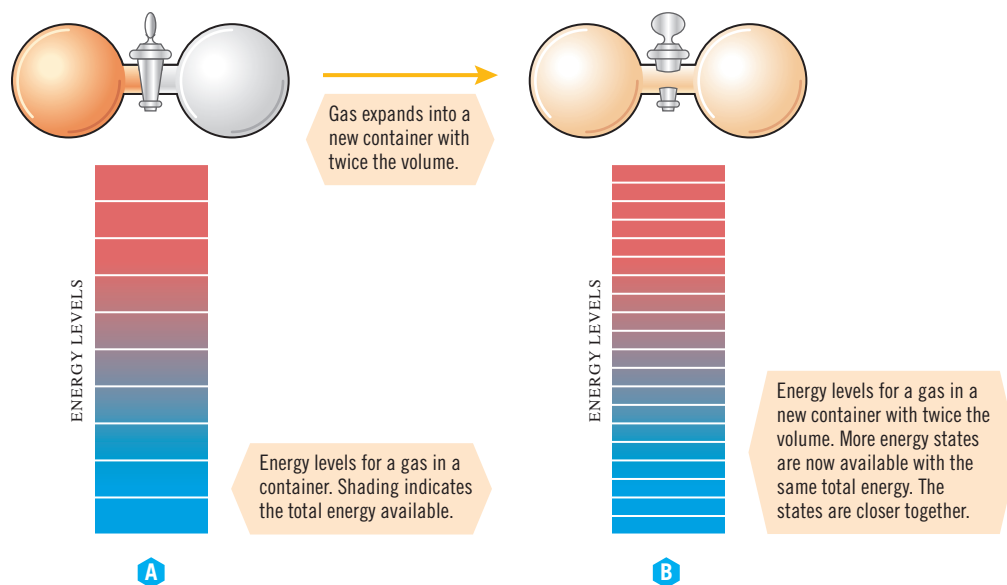


Figure 15-14 Larger gas volumes give more energy levels.

15-14 Entropy, S , and Entropy Change, ΔS

The dispersal of energy and matter is described by the thermodynamic state function **entropy**, S . In the most fundamental description, the greater the energy dispersal in a system, the higher is its entropy. We have said that greater disorder (dispersal of matter, both in space and in variety) can lead to greater dispersal of energy, and hence to higher entropy. This connection allows us to discuss many entropy changes in terms of increases or decreases in the disorder and the energy dispersal of the system. Let us first see how entropy is tabulated and how entropy changes are calculated.

The **Third Law of Thermodynamics** establishes the zero of the entropy scale.

The entropy of a pure, perfect crystalline substance (perfectly ordered) is zero at absolute zero (0 K).

As the temperature of a substance increases, the particles vibrate more vigorously, so the entropy increases (Figure 15-15). Further heat input causes either increased temperature (still higher entropy) or phase transitions (melting, sublimation, or boiling) that also result in higher entropy. The entropy of a substance at any condition is its **absolute entropy**, also called **standard molar entropy**. Consider the absolute entropies at 298 K listed in Table 15-4. At 298 K, *any* substance is more disordered than if it were in a perfect crystalline state at absolute zero, so tabulated S_{298}^0 values for compounds and elements are *always positive*. Notice especially that S_{298}^0 of an element, unlike its ΔH_f^0 , is *not* equal to zero. The reference state for absolute entropy is specified by the Third Law of Thermodynamics. It is different from the reference state for ΔH_f^0 (see Section 15-7). The absolute entropies, S_{298}^0 , of various substances under standard conditions are tabulated in Appendix K.

Just as for other thermodynamic quantities, the entropy change for a system, ΔS_{system} , is the difference between final and initial states:

$$\Delta S_{\text{system}} = S_{\text{system, final}} - S_{\text{system, initial}}$$

The **standard entropy change**, ΔS^0 , of a reaction can be determined from the absolute entropies of reactants and products. The relationship is analogous to Hess's Law.

$$\Delta S_{\text{rxn}}^0 = \sum n S_{\text{products}}^0 - \sum n S_{\text{reactants}}^0$$

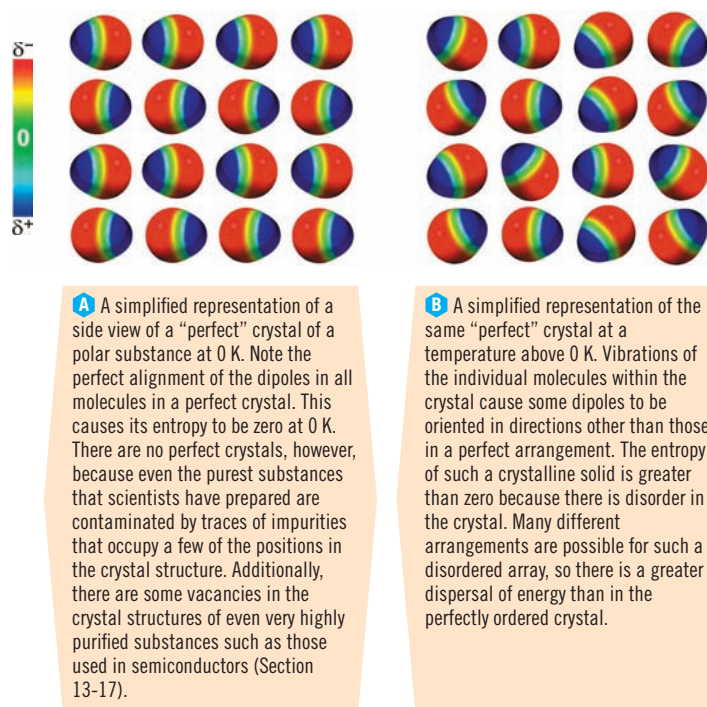
► Enthalpies are measured only as *differences* with respect to an arbitrary standard state. Entropies, in contrast, are defined relative to an absolute zero level. In either case, the *per mole* designation means *per mole of substance in the specified state*.

► The $\sum n$ means that each S^0 value must be multiplied by the appropriate coefficient, n , from the balanced equation. These values are then added.

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 15-4 Absolute Entropies at 298 K for a Few Common Substances

Substance	S^0 (J/mol · K)
C(diamond)	2.38
C(g)	158.0
H ₂ O(l)	69.91
H ₂ O(g)	188.7
I ₂ (s)	116.1
I ₂ (g)	260.6

**Figure 15-15**

S^0 values are tabulated in units of $J/mol \cdot K$ rather than the larger units involving kilojoules that are used for enthalpy changes. The “mol” term in the units for a *substance* refers to a mole of the substance, whereas for a *reaction* it refers to a mole of reaction. Each term in the sums on the right-hand side of the equation has the units

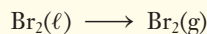
$$\frac{\text{mol substance}}{\text{mol rxn}} \times \frac{J}{(\text{mol substance}) \cdot K} = \frac{J}{(\text{mol rxn}) \cdot K}$$

The result is usually abbreviated as $J/mol \cdot K$, or sometimes even as J/K . As before, we will usually omit units in intermediate steps and then apply appropriate units to the result.

We now illustrate this calculation for a phase change and for a chemical reaction.

EXAMPLE 15-15 Calculation of ΔS^0 for a Phase Change

Use the values of standard molar entropies in Appendix K to calculate the entropy change for the vaporization of one mole of bromine at 25°C.

**Plan**

We use the equation for standard entropy change to calculate ΔS^0 from the tabulated values of standard molar entropies, S^0 , for the final and initial states shown in the process.

Solution

We list the ΔS^0_{298} values from Appendix K:

	$\text{Br}_2(\ell)$	$\text{Br}_2(\text{g})$
$S^0, J/mol \cdot K:$	152.2	245.4

$$\begin{aligned} \Delta S^0 &= \sum n S^0_{\text{products}} - \sum n S^0_{\text{reactants}} \\ &= 1(245.4) - 1(152.2) = 93.2 J/mol \cdot K \end{aligned}$$

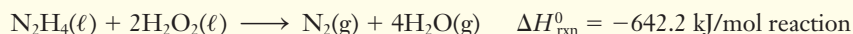
The “mol” designation for $J/mol \cdot K$ refers to a mole of reaction. The reaction as written shows one mole of Br_2 , so this is the entropy change for the vaporization of one mole of Br_2 . It can be called the *molar entropy of vaporization* of Br_2 at 25°C.

STOP & THINK

The matter in a gaseous sample is far more greatly dispersed than in a liquid. Thus vaporization is always accompanied by an increase in entropy ($\Delta S > 0$).

EXAMPLE 15-16 Calculation of ΔS_{rxn}^0 for a Chemical Reaction

Use the values of standard molar entropies in Appendix K to calculate the entropy change at 25°C and one atmosphere pressure for the reaction of hydrazine with hydrogen peroxide. This explosive reaction has been used for rocket propulsion. Do you think the reaction is spontaneous? The balanced equation for the reaction is

**Plan**

We use the equation for standard entropy change to calculate ΔS_{rxn}^0 from the tabulated values of standard molar entropies, S_{298}^0 , for the substances in the reaction.

Solution

We can list the S_{298}^0 values that we obtain from Appendix K for each substance:

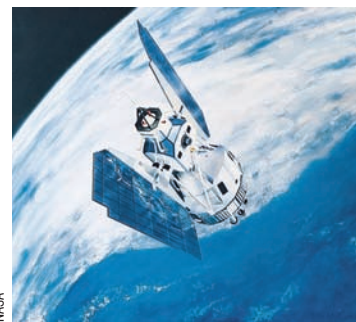
	$\text{N}_2\text{H}_4(\ell)$	$\text{H}_2\text{O}_2(\ell)$	$\text{N}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$
$S^0, \text{ J/mol} \cdot \text{K}$:	121.2	109.6	191.5	188.7

$$\begin{aligned} \Delta S_{\text{rxn}}^0 &= \sum n S_{\text{products}}^0 - \sum n S_{\text{reactants}}^0 \\ &= [S_{\text{N}_2(\text{g})}^0 + 4S_{\text{H}_2\text{O}(\text{g})}^0] - [S_{\text{N}_2\text{H}_4(\ell)}^0 + 2S_{\text{H}_2\text{O}_2(\ell)}^0] \\ &= [1(191.5) + 4(188.7)] - [1(121.2) + 2(109.6)] \end{aligned}$$

$$\Delta S_{\text{rxn}}^0 = +605.9 \text{ J/mol} \cdot \text{K}$$

The “mol” designation for ΔS_{rxn}^0 refers to a mole of reaction, that is, one mole of $\text{N}_2\text{H}_4(\ell)$, two moles of $\text{H}_2\text{O}_2(\ell)$, and so on. Although it may not appear to be, +605.9 J/mol · K is a relatively large value of ΔS_{sys}^0 . The positive entropy change favors spontaneity. This reaction is also exothermic (ΔH^0 is negative). As we shall see, this reaction *must* be spontaneous, because both factors are favorable: the reaction is exothermic (ΔH_{rxn}^0 is negative) and the disorder of the system increases (ΔS_{rxn}^0 is positive).

You should now work Exercise 104.



Small booster rockets adjust the course of a satellite in orbit. Some of these small rockets are powered by the $\text{N}_2\text{H}_4\text{--H}_2\text{O}_2$ reaction.

STOP & THINK

In this reaction, liquid reactants are converted into a larger number of moles of gaseous products. Thus it is reasonable that entropy increases ($\Delta S^0 > 0$).

Because changes in the thermodynamic quantity *entropy* may be understood in terms of changes in *energy dispersal* and *molecular disorder*, we can often predict the sign of ΔS_{sys} . The following illustrations emphasize several common types of processes that result in predictable entropy changes for the system.

Phase changes. In a solid, the molecules are in an ordered arrangement, where they can vibrate only around their relatively fixed positions. In a liquid, the molecules are more disordered, so they exchange energy much more freely, and the entropy is higher than in the solid. Similarly, gas molecules are in a much larger volume, and they are far less restrained than in the liquid. In the gas, they move even more randomly, both in direction and in speed; this gives any substance a much higher entropy as a gas than as a liquid or a solid (Figure 15-16). Thus the processes of melting, vaporization, and sublimation are always accompanied by an increase in entropy (Figure 15-17). The reverse processes of freezing, condensation, and deposition always correspond to a decrease in entropy.

For any substance, entropy increases in the order solid < liquid < gas.

Melting, vaporization, and sublimation always have $\Delta S_{\text{system}} > 0$.

Freezing, condensation, and deposition always have $\Delta S_{\text{system}} < 0$.

Temperature changes. As the temperature of any sample increases, its molecules have increased total kinetic energy; this higher energy can be dispersed among these molecules in more ways, increasing the entropy of the sample. Furthermore, the greater motion of the molecules (translational for gases and liquids, vibrational for solids) corresponds to a state

Unless otherwise noted, all content on this page is © Cengage Learning.

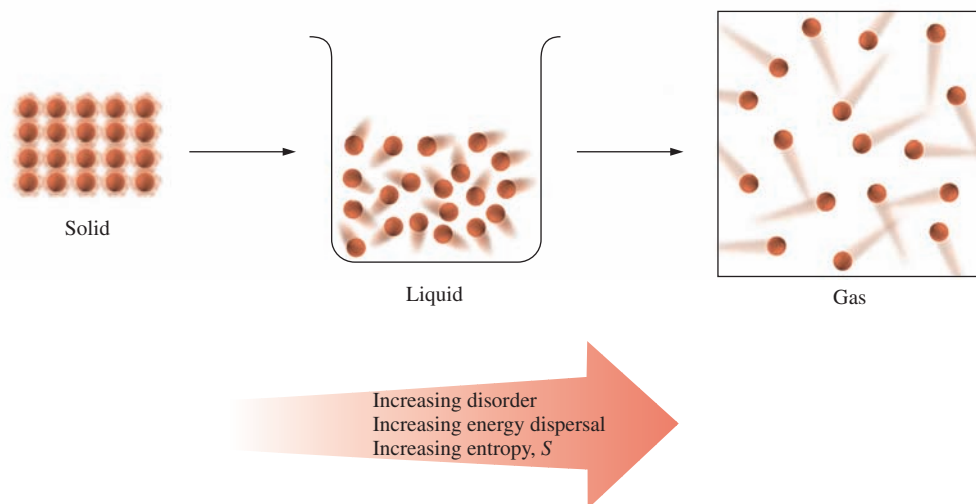


Figure 15-16 As a sample changes from solid to liquid to gas, its particles become increasingly more disordered, allowing greater dispersal of energy, so its entropy increases.

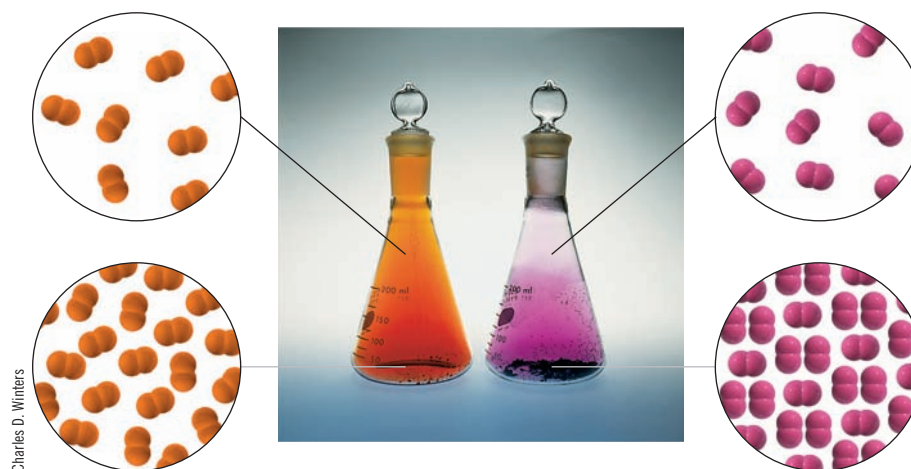


Figure 15-17 The vaporization of bromine, $\text{Br}_2(\ell) \rightarrow \text{Br}_2(\text{g})$ (left) and the sublimation of iodine, $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$ (right) both lead to an increase in disorder, so $\Delta S_{\text{sys}} > 0$ for each process. Which do you think results in the more positive ΔS ? Carry out the calculation using values from Appendix K to check whether your prediction was correct.

of greater matter dispersal. The increased dispersal of matter and energy leads to the following result.

The entropy of any sample increases as its temperature increases.

Volume changes. When the volume of a sample of gas increases, the molecules can occupy more positions, and hence are more randomly arranged (greater dispersal of matter). As pointed out in Section 15-13, the energy levels available to the molecules are closer together in the larger volume, leading to more ways to distribute the same total energy (greater dispersal of energy). Thus a gas has higher entropy at higher volume.

The entropy of a gas increases as its volume increases.
For an increase in gas volume, $\Delta S_{\text{system}} > 0$.

Mixing of substances, even without chemical reaction. Situations in which particles of more than one kind are “mixed up” are more disordered (greater dispersal of matter) and can exchange energy among both like and unlike particles (greater dispersal of energy). The entropy of the mixture is thus greater than that of the individual substances. This increase in entropy favors processes such as the mixing of gases (see Figure 15-10) and the dissolving of solid and liquid solutes in liquid solvents (Figures 15-18 and 15-19; see also Section 14-2). For example, when one mole of solid NaCl dissolves in water, $\text{NaCl(s)} \longrightarrow \text{NaCl(aq)}$, the entropy (Appendix K) increases from $72.4 \text{ J/mol} \cdot \text{K}$ to $115.5 \text{ J/mol} \cdot \text{K}$, or $\Delta S^\circ = +43.1 \text{ J/mol} \cdot \text{K}$. The term “mixing” can be interpreted rather liberally. For example, the reaction $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl(g)}$ has $\Delta S^\circ > 0$; in the reactants, each atom is bonded to an identical atom, a less “mixed-up” situation than in the products, where unlike atoms are bonded together.

Mixing of substances or dissolving a solid in a liquid causes an increase in entropy, $\Delta S_{\text{system}} > 0$.

Changes in the number of particles, as in the dissociation of a diatomic gas such as $\text{F}_2(\text{g}) \longrightarrow 2\text{F(g)}$. Any process in which the number of particles increases results in an increase in entropy, $\Delta S_{\text{sys}} > 0$. Values of ΔS° calculated for several reactions of this type are given in Table 15-5. As you can see, the ΔS° values for the dissociation process $\text{X}_2 \longrightarrow 2\text{X}$ are all similar for $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{and N}$. Why is the value given in Table 15-5 so much larger for $\text{X} = \text{Br}$? This process starts with *liquid* Br_2 . The total process $\text{Br}_2(\ell) \longrightarrow 2\text{Br(g)}$, for which $\Delta S^\circ = 197.6 \text{ J/mol} \cdot \text{K}$, can be treated as the result of *two* processes. The first of these is *vaporization*, $\text{Br}_2(\ell) \longrightarrow \text{Br}_2(\text{g})$, for which $\Delta S^\circ = 93.2 \text{ J/mol} \cdot \text{K}$. The second step is the dissociation of gaseous bromine, $\text{Br}_2(\text{g}) \longrightarrow 2\text{Br(g)}$, for

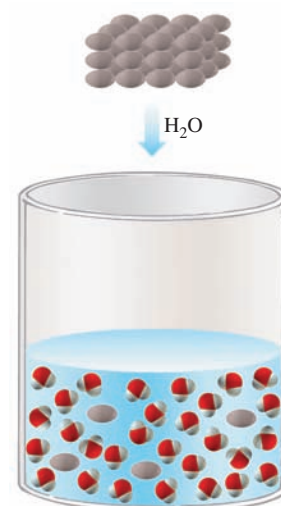


Figure 15-18 As particles leave a crystal to go into solution, they become more disordered and energy dispersal increases. This favors dissolution of the solid.

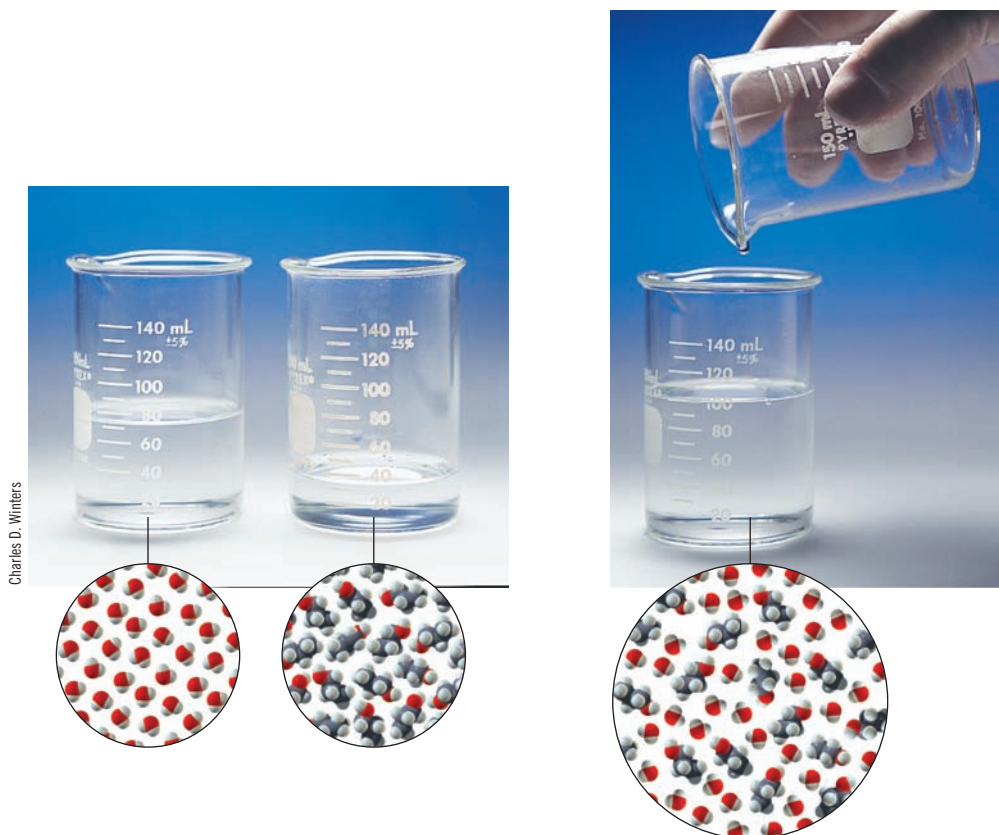


Figure 15-19 When water, H_2O , and propyl alcohol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (left) are mixed to form a solution (right), disorder increases. $\Delta S > 0$ for the mixing of any two molecular substances.

Table 15-5 Entropy Changes for Some Processes $X_2 \longrightarrow 2X$

Reaction	ΔS° (J/mol · K)
$H_2(g) \longrightarrow 2H(g)$	98.0
$N_2(g) \longrightarrow 2N(g)$	114.9
$O_2(g) \longrightarrow 2O(g)$	117.0
$F_2(g) \longrightarrow 2F(g)$	114.5
$Cl_2(g) \longrightarrow 2Cl(g)$	107.2
$Br_2(l) \longrightarrow 2Br(g)$	197.6
$I_2(s) \longrightarrow 2I(g)$	245.3

► Do you think that the reaction $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ would have a higher or lower value of ΔS° than when the water is in the gas phase? Confirm by calculation.

which $\Delta S^\circ = 104.4 \text{ J/mol} \cdot \text{K}$; this entropy increase is about the same as for the other processes that involve *only* dissociation of a gaseous diatomic species. Can you rationalize the even higher value given in the table for the process $I_2(s) \longrightarrow 2I(g)$?

Increasing the number of particles causes an increase in entropy, $\Delta S_{\text{system}} > 0$.

Changes in the number of moles of gaseous substances. Processes that result in an increase in the number of moles of gaseous substances have $\Delta S_{\text{sys}} > 0$. Example 15-16 illustrates this. There are no gaseous reactants, but the products include five moles of gas. Conversely, we would predict that the process $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$ has a negative ΔS° value; here, three moles of gas is consumed while only two moles is produced, for a net decrease in the number of moles in the gas phase. You should be able to calculate the value of ΔS° for this reaction from the values in Appendix K.

An increase in the number of moles of gaseous substances causes an increase in entropy, $\Delta S_{\text{system}} > 0$.

The following guidelines for absolute entropy (standard molar entropy) for individual substances can also be helpful in predicting entropy changes.

Molecular size and complexity. For molecules with similar formulas, absolute entropies usually increase with increasing molecular weight. For instance, the entropies of the gaseous hydrogen halide increase in the order $HF (173.7 \text{ J/mol} \cdot \text{K}) < HCl (186.8 \text{ J/mol} \cdot \text{K}) < HBr (198.59 \text{ J/mol} \cdot \text{K}) < HI (206.5 \text{ J/mol} \cdot \text{K})$. In more complicated molecular structures, there are more ways for the atoms to move about in three-dimensional space, so there is greater entropy. This trend is especially strong for a series of related compounds. For instance, the absolute entropy of liquid hydrogen peroxide, H_2O_2 ($109.6 \text{ J/mol} \cdot \text{K}$), is greater than that of liquid water, H_2O ($69.91 \text{ J/mol} \cdot \text{K}$). Gaseous PCl_5 has a greater absolute entropy ($353 \text{ J/mol} \cdot \text{K}$) than gaseous PCl_3 ($311.7 \text{ J/mol} \cdot \text{K}$). Note that molecular complexity and molecular weight play an increasingly important role in the entropy when comparing molecules. For example, gases usually have the highest entropy values when comparing molecules of similar molecular weight. But a solid with a high molecular weight and complexity can have a higher entropy than a lighter gas. Solid sucrose ($C_{12}H_{22}O_{11}$; MW = 342 g/mol) has $S^\circ = 392 \text{ J/mol}$, whereas $PCl_5(g)$ (MW = 208 g/mol) has a lower entropy of 353 J/mol .

Ionic compounds with similar formulas but different charges. Stronger ionic attractions (due to higher charges or closer approach) hold the ions more tightly in their crystal positions, so they vibrate less, leading to lower entropy. For instance, CaS and KCl have similar formula weights; but CaS ($2+$ and $2-$ ionic charges) has stronger ionic attractive forces than KCl ($1+$, $1-$ charges), consistent with their relative entropies $CaS (56.5 \text{ J/mol} \cdot \text{K}) < KCl (82.6 \text{ J/mol} \cdot \text{K})$.

Problem-Solving Tip

Of the factors just listed, *changes in number of particles* and *changes in number of moles of gas* are usually the most important factors in predicting the sign of an entropy change for a reaction.

EXAMPLE 15-17 Predicting the Sign of ΔS° for a Chemical Reaction

Without doing a calculation, predict whether the entropy change will be positive or negative when each reaction occurs in the direction it is written.

- $C_2H_6(g) + \frac{7}{2} O_2(g) \longrightarrow 3H_2O(g) + 2CO_2(g)$
- $3C_2H_2(g) \longrightarrow C_6H_6(l)$
- $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$

Plan

We use the qualitative guidelines described above to predict whether entropy increases or decreases.

Solution

- (a) In this reaction, 9/2 moles (4.5 moles) of gaseous reactants produce 5 moles of gaseous products. This increase in number of moles of gas leads to an increase in entropy, $\Delta S^0 > 0$.
- (b) Here 3 moles of gaseous reactants produce only liquid product. This decrease in number of moles of gas leads to a decrease in entropy, $\Delta S^0 < 0$.
- (c) In this reaction, there are 6 moles of gaseous reactants and the same number of moles of gaseous products, so the prediction cannot be made on this basis. One of the reactants, $C_6H_{12}O_6$, is a solid. The total entropy of one mole of solid and six moles of gas (reactants) is less than the total entropy of six moles of gas and six moles of liquid (products), so we predict an increase in entropy, $\Delta S^0 > 0$.

You should now work Exercise 100.

STOP & THINK

You can apply this kind of reasoning to help you judge whether a calculated entropy change has the correct sign.

EXAMPLE 15-18 Predicting the Order of Absolute Entropies

Rank each group of substances in order of increasing absolute entropy at 25°C. Give reasons for your ranking.

- (a) $Hg(\ell)$, $Hg(s)$, $Hg(g)$
- (b) $C_2H_6(g)$, $CH_4(g)$, $C_3H_8(g)$
- (c) $CaS(s)$, $CaO(s)$

Plan

We use the qualitative comparisons of this section to rank the absolute entropies within each group.

Solution

- (a) For any substance, entropy increases in the order solid < liquid < gas, so we predict the absolute entropies to increase as $Hg(s) < Hg(\ell) < Hg(g)$.
- (b) Entropy increases with molecular complexity, so we predict the absolute entropies to increase in the order $CH_4(g) < C_2H_6(g) < C_3H_8(g)$.
- (c) Both of these ionic compounds contain $2+$ and $2-$ ions, so charge differences alone will not allow us to rank them. But O^{2-} ions are smaller than S^{2-} ions, so they are held closer to the Ca^{2+} ions, giving a stronger attraction in CaO and hence lower entropy. We expect the absolute entropies to increase in the order $CaO(s) < CaS(s)$.

You should now work Exercise 98.

► You can check the rankings in Example 15-18 by comparing the S^0 values listed in Appendix K.

15-15 The Second Law of Thermodynamics

We now know that two factors determine whether a reaction is spontaneous under a given set of conditions. The effect of the first factor, the enthalpy change, is that spontaneity is favored (but not required) by exothermicity, and nonspontaneity is favored (but not required) by endothermicity. The effect of the other factor is summarized by the **Second Law of Thermodynamics**.

In any spontaneous change, entropy of the universe increases, $\Delta S_{\text{universe}} > 0$.

The Second Law of Thermodynamics is based on our experiences, as seen by the following examples. Gases mix spontaneously. When a drop of food coloring is added to a glass of water, it diffuses until a homogeneously colored solution results. When a truck is driven down the street, it consumes fuel and oxygen, producing carbon dioxide, water vapor, and other emitted substances.

Unless otherwise noted, all content on this page is © Cengage Learning.



The reverse of any spontaneous change is nonspontaneous, because if it did occur, the universe would tend toward a state of lower entropy (greater order, more concentration of energy). This is contrary to our experience. A gas mixture does not spontaneously separate into its components. A colored solution does not spontaneously concentrate all of its color in a small volume. A truck cannot be driven along the street, even in reverse gear, so that it sucks up CO_2 , water vapor, and other substances to produce fuel and oxygen.

If the entropy of a system increases during a process, the spontaneity of the process is favored but not required. The Second Law of Thermodynamics says that the entropy of the *universe* (but not necessarily the system) increases during a spontaneous process, that is,

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \quad (\text{spontaneous process})$$

Of the two ideal gas samples in Figure 15-10, the more ordered arrangement (Figure 15-10a) has lower entropy than the randomly mixed arrangement with the same volume (Figure 15-10b). Because these ideal gas samples mix without absorbing or releasing heat and without a change in total volume, they do not interact with the surroundings, so the entropy of the surroundings does not change. In this case

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}}$$

If we open the stopcock between the two bulbs in Figure 15-10a, we expect the gases to mix spontaneously, with an increase in the disorder of the system, that is, ΔS_{system} is positive.

$$\text{unmixed gases} \longrightarrow \text{mixed gases} \quad \Delta S_{\text{universe}} = \Delta S_{\text{system}} > 0$$

We do not expect the more homogeneous sample in Figure 15-10b to spontaneously “unmix” to give the arrangement in Figure 15-10a (which would correspond to a decrease in ΔS_{system}).

$$\text{mixed gases} \longrightarrow \text{unmixed gases} \quad \Delta S_{\text{universe}} = \Delta S_{\text{system}} < 0$$

► We abbreviate these subscripts as follows: system = sys, surroundings = surr, and universe = univ.

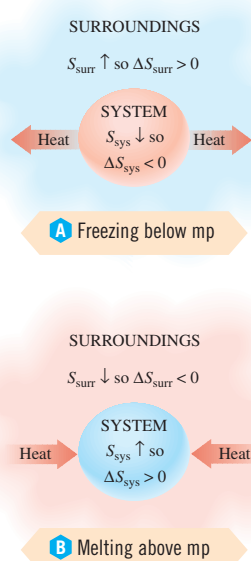


Figure 15-20 A schematic representation of heat flow and entropy changes for (a) freezing and (b) melting of a pure substance.

The entropy of a system can decrease during a spontaneous process or increase during a nonspontaneous process, depending on the accompanying ΔS_{surr} . If ΔS_{sys} is negative (decrease in disorder), then ΔS_{univ} may still be positive (overall increase in disorder) if ΔS_{surr} is more positive than ΔS_{sys} is negative. A refrigerator provides an illustration. It removes heat from inside the box (the system) and ejects that heat, *plus* the heat generated by the compressor, into the room (the surroundings). The entropy of the system decreases because the air molecules inside the box move more slowly. But the increase in the entropy of the surroundings more than makes up for that, so the entropy of the universe (refrigerator + room) increases.

Similarly, if ΔS_{sys} is positive but ΔS_{surr} is even more negative, then ΔS_{univ} is still negative. Such a process will be nonspontaneous.

Let's consider the entropy changes that occur when a liquid solidifies at a temperature *below* its freezing (melting) point (Figure 15-20a). ΔS_{sys} is negative because a solid forms from its liquid, yet we know that this is a spontaneous process. A liquid releases heat to its surroundings (atmosphere) as it crystallizes. The released heat increases the motion (more disorder, greater dispersal of matter) of the molecules of the surroundings, so ΔS_{surr} is positive. As the temperature decreases, the ΔS_{surr} contribution becomes more important. When the temperature is low enough (below the freezing point), the positive ΔS_{surr} outweighs the negative ΔS_{sys} . Then ΔS_{univ} becomes positive, and the freezing process becomes spontaneous.

The situation is reversed when a liquid is boiled or a solid is melted (see Figure 15-20b). For example, at temperatures above its melting point, a solid spontaneously melts, the system becomes more disordered (greater dispersal of matter), and ΔS_{sys} is positive. The heat absorbed when the solid (system) melts comes from its surroundings. This decreases the motion of the molecules of the surroundings. Thus, ΔS_{surr} is negative (the surroundings become less disordered). The positive ΔS_{sys} is greater in magnitude than the negative ΔS_{surr} ; however, so ΔS_{univ} is positive and the process is spontaneous.

Above the melting point, ΔS_{univ} is positive for melting. Below the melting point, ΔS_{univ} is positive for freezing. At the melting point, ΔS_{surr} is equal in magnitude and opposite in

Table 15-6 Entropy Effects Associated with Melting and Freezing

Change	Temperature	Sign of		(Magnitude of ΔS_{sys}) Compared with (Magnitude of ΔS_{surr})	$\Delta S_{\text{univ}} =$ $\Delta S_{\text{sys}} + \Delta S_{\text{surr}}$	Spontaneity
		ΔS_{sys}	ΔS_{surr}			
1. Melting (solid $\rightarrow$ liquid)	$> \text{mp}$	+	−	$>$	> 0	Spontaneous
	$= \text{mp}$	+	−	$=$	$= 0$	Equilibrium
	$< \text{mp}$	+	−	$<$	< 0	Nonspontaneous
2. Freezing (liquid $\rightarrow$ solid)	$> \text{mp}$	−	+	$>$	< 0	Nonspontaneous
	$= \text{mp}$	−	+	$=$	$= 0$	Equilibrium
	$< \text{mp}$	−	+	$<$	> 0	Spontaneous

sign to ΔS_{sys} . Then ΔS_{univ} is zero for both melting and freezing; the system is at *equilibrium*. Table 15-6 lists the entropy effects for these changes of physical state.

We have said that ΔS_{univ} is positive for all spontaneous (product-favored) processes. Unfortunately, it is not possible to make direct measurements of ΔS_{univ} . Consequently, entropy changes accompanying physical and chemical changes are reported in terms of ΔS_{sys} . The subscript “sys” for system can be replaced with rxn if we wish to indicate a chemical reaction. The symbol ΔS_{rxn} refers to the change in entropy of a reacting system, just as ΔH_{rxn} refers to the change in enthalpy of the reacting system.

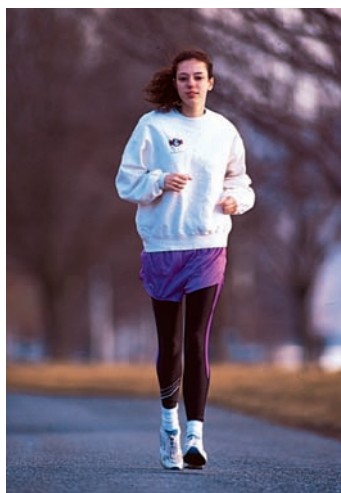
► Can you develop a comparable table for boiling (liquid $\rightarrow$ gas) and condensation (gas $\rightarrow$ liquid)? (Study Table 15-6 carefully.)

15-16 Free Energy Change, ΔG , and Spontaneity

Energy is the capacity to do work. If heat is released in a chemical reaction (ΔH is negative), *some* of the heat energy may be converted into useful work. If ΔS is negative, some of the energy must be expended to increase the order of the system. If the system becomes more disordered ($\Delta S > 0$), however, more useful energy becomes available than indicated by ΔH alone. J. Willard Gibbs (1839–1903), a prominent 19th-century American professor



Dennis Dreimer



A The entropy of an organism decreases (unfavorable) when new cells are formed. The energy to sustain animal life is provided by the metabolism of food. This energy is released when the chemical bonds in the food are broken. Exhalation of gases and excretion of waste materials increase the entropy of the surroundings enough so that the entropy of the universe increases and the overall process can occur.

B Stored chemical energy can later be transformed by the organism to the mechanical energy for muscle contraction, to the electrical energy for brain function, or to another needed form.

► Entropy plays an important role in the energy transfer in cell growth and maintenance in all living organisms.

of mathematics and physics, formulated the relationship between enthalpy and entropy in terms of another state function that we now call the **Gibbs free energy**, G . It is defined as

$$G = H - TS$$

The **Gibbs free energy change**, ΔG , at constant temperature and pressure, is

$$\Delta G = \Delta H - T\Delta S \quad (\text{constant } T \text{ and } P)$$

► This is often called simply the *Gibbs energy change* or the *free energy change*.

The amount by which the Gibbs free energy decreases is the *maximum useful energy* obtainable in the form of work from a given process at constant temperature and pressure. It is also the *indicator of spontaneity of a reaction or physical change* at constant T and P . If there is a net decrease of free energy, ΔG is negative and the process is spontaneous (product-favored). We see from the equation that ΔG becomes more negative as (1) ΔH becomes more negative (the process gives off more heat) and (2) ΔS becomes more positive (the process results in greater disorder); *both* factors are favorable so the process *must be* spontaneous (product-favored). If there is a net increase in free energy of the system during a process, ΔG is positive and the process is nonspontaneous (reactant-favored). This means that the reverse process is spontaneous under the given conditions. When $\Delta G = 0$, there is no net transfer of free energy; both the forward and reverse processes are equally favorable. Thus, $\Delta G = 0$ describes a system at *equilibrium*.

The relationship between ΔG and spontaneity may be summarized as follows.

ΔG	Spontaneity of Reaction (constant T and P)
ΔG is positive	Reaction is nonspontaneous (reactant-favored)
ΔG is zero	System is at equilibrium
ΔG is negative	Reaction is spontaneous (product-favored)

—	0	+
$\Delta G < 0$		$\Delta G > 0$
Reaction is spontaneous		Reaction is not spontaneous
Product-favored reaction		Reactant-favored reaction
Forward reaction is favored		Reverse reaction is favored

The free energy content of a system depends on temperature and pressure (and, for mixtures, on concentrations). The value of ΔG for a process depends on the states and the concentrations of the various substances involved. It also depends strongly on temperature, because the equation $\Delta G = \Delta H - T\Delta S$ includes temperature. Just as for other thermodynamic variables, we choose some set of conditions as a standard state reference. The standard state for ΔG^0 is the same as for ΔH^0 ; 1 atm and the specified temperature, usually 25°C (298 K). Values of standard molar free energy of formation, ΔG_f^0 , for many substances are tabulated in Appendix K. For *elements* in their standard states, $\Delta G_f^0 = 0$. The values of ΔG_f^0 may be used to calculate the standard free energy change of a reaction at 298 K by using the following relationship.

$$\Delta G_{\text{rxn}}^0 = \sum n \Delta G_{\text{f products}}^0 - \sum n \Delta G_{\text{f reactants}}^0 \quad (1 \text{ atm and } 298 \text{ K only})$$

► We want to know which are more stable at standard conditions—the reactants or the products.

The value of ΔG_{rxn}^0 allows us to predict the spontaneity of a hypothetical reaction in which the numbers of moles of reactants shown in the balanced equation, all at standard conditions, are *completely* converted to the numbers of moles of products shown in the balanced equation, all at standard conditions.

We must remember that it is ΔG , and not ΔG^0 , that is the general criterion for spontaneity. ΔG depends on concentrations of reactants and products in the mixture. For most reactions, there is an *equilibrium mixture* of reactant and product concentrations that is more stable than either all reactants or all products. In Chapter 17 we will study the concept of equilibrium and see how to find ΔG for mixtures.

EXAMPLE 15-19 Spontaneity of Reaction

Diatomic nitrogen and oxygen molecules make up about 99% of all the molecules in reasonably “unpolluted” dry air. Evaluate ΔG^0 for the following reaction at 298 K, using ΔG_f^0 values from Appendix K. Is the reaction spontaneous?



Plan

The reaction conditions are 1 atm and 298 K, so we can use the tabulated values of ΔG_f^0 for each substance in Appendix K to evaluate ΔG_{rxn}^0 in the preceding equation. The treatment of units for calculation of ΔG^0 is the same as that for ΔH^0 in Example 15-9.

Solution

We obtain the following values of ΔG_f^0 from Appendix K:

	$\text{N}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{NO}(\text{g})$	
$\Delta G_f^0, \text{kJ/mol:}$	0	0		86.57

$$\begin{aligned} \Delta G_{\text{rxn}}^0 &= \sum n \Delta G_f^0 \text{ products} - \sum n \Delta G_f^0 \text{ reactants} \\ &= 2 \Delta G_f^0 \text{ NO}(\text{g}) - [\Delta G_f^0 \text{ N}_2(\text{g}) + \Delta G_f^0 \text{ O}_2(\text{g})] \\ &= 2(86.57) - [0 + 0] \\ \Delta G_{\text{rxn}}^0 &= +173.1 \text{ kJ/mol rxn} \quad \text{for the reaction as written} \end{aligned}$$

Because ΔG^0 is positive, the reaction is nonspontaneous at 298 K under standard state conditions.

You should now work Exercise 111.

The value of ΔG^0 can also be calculated by the equation

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (\text{constant } T \text{ and } P)$$

Strictly, this last equation applies to standard conditions; however, ΔH^0 and ΔS^0 often do not vary much with temperature, so the equation can often be used to *estimate* free energy changes at other temperatures.

► For the reverse reaction at 298 K, $\Delta G_{\text{rxn}}^0 = -173.1 \text{ kJ/mol rxn}$. So the reverse reaction is product-favored, although it is very slow at room temperature. The NO formed in automobile engines is oxidized to even more harmful NO_2 much more rapidly than it decomposes to N_2 and O_2 . Thermodynamic spontaneity does not guarantee that a process occurs at an observable rate. The oxides of nitrogen in the atmosphere represent a major environmental problem.



Problem-Solving Tip Some Common Pitfalls in Calculating ΔG_{rxn}^0

Be careful of these points when you carry out calculations that involve ΔG^0 :

1. The calculation of ΔG_{rxn}^0 from tabulated values of ΔG_f^0 is valid *only* for the reaction at 25°C (298 K) and one atmosphere.
2. Calculations with the equation $\Delta G^0 = \Delta H^0 - T \Delta S^0$ must be carried out with the temperature in kelvins.
3. The energy term in ΔS^0 is usually in joules, whereas that in ΔH^0 is usually in kilojoules; remember to convert one of these so that units are consistent before you combine them.

EXAMPLE 15-20 Spontaneity of Reaction

Make the same determination as in Example 15-19, using heats of formation and absolute entropies rather than free energies of formation.

Plan

First we calculate ΔH_{rxn}^0 and ΔS_{rxn}^0 . We use the relationship $\Delta G^0 = \Delta H^0 - T \Delta S^0$ to evaluate the free energy change under standard state conditions at 298 K.

Solution

The values we obtain from Appendix K are

	$\text{N}_2(\text{g})$	$\text{O}_2(\text{g})$	$\text{NO}(\text{g})$
$\Delta H_f^0, \text{kJ/mol}$:	0	0	90.25
$S^0, \text{J/mol} \cdot \text{K}$:	191.5	205.0	210.7
$\Delta H_{\text{rxn}}^0 = \sum n \Delta H_{\text{f products}}^0 - \sum n \Delta H_{\text{f reactants}}^0$			
$= 2 \Delta H_{\text{f NO(g)}}^0 - [\Delta H_{\text{f N}_2(\text{g})}^0 + \Delta H_{\text{f O}_2(\text{g})}^0]$			
$= [2(90.25) - (0 + 0)] = 180.5 \text{ kJ/mol}$			
$\Delta S_{\text{rxn}}^0 = \sum n S_{\text{products}}^0 - \sum n S_{\text{reactants}}^0$			
$= 2S_{\text{NO(g)}}^0 - [S_{\text{N}_2(\text{g})}^0 + S_{\text{O}_2(\text{g})}^0]$			
$= [2(210.7) - (191.5 + 205.0)] = 24.9 \text{ J/mol} \cdot \text{K} = 0.0249 \text{ kJ/mol} \cdot \text{K}$			

Now we use the relationship $\Delta G^0 = \Delta H^0 - T \Delta S^0$, with $T = 298 \text{ K}$, to evaluate the free energy change under standard state conditions at 298 K.

$$\begin{aligned}\Delta G_{\text{rxn}}^0 &= \Delta H_{\text{rxn}}^0 - T \Delta S_{\text{rxn}}^0 \\ &= 180.5 \text{ kJ/mol} - (298 \text{ K})(0.0249 \text{ kJ/mol} \cdot \text{K}) \\ &= 180.5 \text{ kJ/mol} - 7.42 \text{ kJ/mol}\end{aligned}$$

$$\Delta G_{\text{rxn}}^0 = +173.1 \text{ kJ/mol rxn, the same value obtained in Example 15-19.}$$

You should now work Exercise 113.

STOP & THINK

As with all calculations of ΔG , you should be careful to make the energy units in ΔH and ΔS consistent—either both in J or both in kJ.

15-17 The Temperature Dependence of Spontaneity

The methods developed in Section 15-16 can also be used to estimate the temperature at which a process is in equilibrium. When a system is at equilibrium, $\Delta G = 0$. Thus,

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T \Delta S_{\text{rxn}} \quad \text{or} \quad 0 = \Delta H_{\text{rxn}} - T \Delta S_{\text{rxn}}$$

so

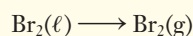
$$\Delta H_{\text{rxn}} = T \Delta S_{\text{rxn}} \quad \text{or} \quad T = \frac{\Delta H_{\text{rxn}}}{\Delta S_{\text{rxn}}} \quad (\text{at equilibrium})$$

EXAMPLE 15-21 Estimation of Boiling Point

Use the thermodynamic data in Appendix K to estimate the normal boiling point of bromine, Br_2 . Assume that ΔH and ΔS do not change with temperature.

Plan

The process we must consider is



▶ Actually, both ΔH_{rxn}^0 and ΔS_{rxn}^0 vary with temperature, but usually not enough to introduce significant errors for modest temperature changes. The value of ΔG_{rxn}^0 , on the other hand, is strongly dependent on the temperature.

Unless otherwise noted, all content on this page is © Cengage Learning.

By definition, the normal boiling point of a liquid is the temperature at which pure liquid and pure gas coexist in equilibrium at 1 atm. Therefore, $\Delta G = 0$ for the process as written. We assume that $\Delta H_{\text{rxn}} = \Delta H_{\text{rxn}}^0$ and $\Delta S_{\text{rxn}} = \Delta S_{\text{rxn}}^0$. We can evaluate these two quantities, substitute them in the relationship $\Delta G = \Delta H - T \Delta S$, and then solve for the value of T that makes $\Delta G = 0$.

Solution

The required values (see Appendix K) are as follows:

	$\text{Br}_2(\ell)$	$\text{Br}_2(\text{g})$
ΔH_f^0 , kJ/mol:	0	30.91
S^0 , J/mol · K:	152.2	245.4

$$\Delta H_{\text{rxn}} = \Delta H_{\text{f Br}_2(\text{g})}^0 - \Delta H_{\text{f Br}_2(\ell)}^0$$

$$= 30.91 - 0 = 30.91 \text{ kJ/mol}$$

$$\Delta S_{\text{rxn}} = S_{\text{Br}_2(\text{g})}^0 - S_{\text{Br}_2(\ell)}^0$$

$$= (245.4 - 152.2) = 93.2 \text{ J/mol} \cdot \text{K} = 0.0932 \text{ kJ/mol} \cdot \text{K}$$

We can now solve for the temperature at which the system is in equilibrium, that is, the boiling point of Br_2 .

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T \Delta S_{\text{rxn}} = 0 \quad \text{so} \quad \Delta H_{\text{rxn}} = T \Delta S_{\text{rxn}}$$

$$T = \frac{\Delta H_{\text{rxn}}}{\Delta S_{\text{rxn}}} = \frac{30.91 \text{ kJ/mol}}{0.0932 \text{ kJ/mol} \cdot \text{K}} = 332 \text{ K } (59^\circ\text{C})$$

This is the temperature at which the reactant (liquid) is in equilibrium with the product (gas), that is, the boiling point of Br_2 . The experimentally measured value is 58.78°C .

You should now work Exercise 122.

STOP & THINK

Remember to use the same energy units in ΔS^0 and ΔH^0 .

The free energy change and spontaneity of a reaction depend on both enthalpy and entropy changes. Both ΔH and ΔS may be either positive or negative, so we can group reactions in four classes with respect to spontaneity (Figure 15-21).

$\Delta G = \Delta H - T \Delta S$		(constant temperature and pressure)
1. $\Delta H = -$ (favorable)	$\Delta S = +$ (favorable)	Reactions are spontaneous (product-favored) at all temperatures
2. $\Delta H = -$ (favorable)	$\Delta S = -$ (unfavorable)	Reactions become spontaneous (product-favored) below a definite temperature
3. $\Delta H = +$ (unfavorable)	$\Delta S = +$ (favorable)	Reactions become spontaneous (product-favored) above a definite temperature
4. $\Delta H = +$ (unfavorable)	$\Delta S = -$ (unfavorable)	Reactions are nonspontaneous (reactant-favored) at all temperatures

When ΔH and ΔS have opposite signs (classes 1 and 4), they act in the same direction, so the direction of spontaneous change does not depend on temperature. When ΔH and ΔS have the same signs (classes 2 and 3), their effects oppose one another, so changes in temperature can cause one factor or the other to dominate, and spontaneity depends on temperature. For class 2, decreasing the temperature decreases the importance of the *unfavorable* $T \Delta S$ term, so the reaction becomes spontaneous at lower temperatures. For class 3, increasing the temperature increases the importance of the *favorable* $T \Delta S$ term, so the reaction becomes spontaneous at higher temperatures.

Unless otherwise noted, all content on this page is © Cengage Learning.

The temperature at which $\Delta G_{\text{rxn}}^0 = 0$ is the temperature limit of spontaneity. The sign of ΔS_{rxn}^0 tells us whether the reaction is spontaneous *below* or *above* this limit (Table 15-7). We can estimate the temperature range over which a chemical reaction in class 2 or 3 is spontaneous by evaluating ΔH_{rxn}^0 and ΔS_{rxn}^0 from tabulated data.

Figure 15-21 A graphical representation of the dependence of ΔG and spontaneity on temperature for each of the four classes of reactions listed in the text and in Table 15-7.

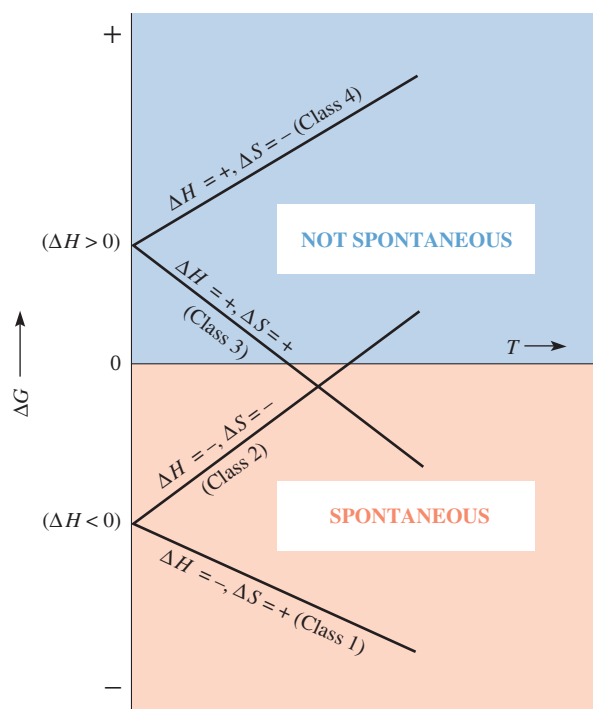
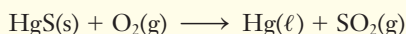


Table 15-7 Thermodynamic Classes of Reactions

Class	Examples	ΔH (kJ/mol)	ΔS (J/mol · K)	Temperature Range of Spontaneity
1	$2\text{H}_2\text{O}_2(\ell) \longrightarrow 2\text{H}_2\text{O}(\ell) + \text{O}_2(\text{g})$ $\text{H}_2(\text{g}) + \text{Br}_2(\ell) \longrightarrow 2\text{HBr}(\text{g})$	-196 -72.8	+126 +114	All temperatures All temperatures
2	$\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{s})$ $2\text{H}_2\text{S}(\text{g}) + \text{SO}_2(\text{g}) \longrightarrow 3\text{S}(\text{s}) + 2\text{H}_2\text{O}(\ell)$	-176 -233	-285 -424	Lower temperatures (< 619 K) Lower temperatures (< 550 K)
3	$\text{NH}_4\text{Cl}(\text{s}) \longrightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ $\text{CCl}_4(\ell) \longrightarrow \text{C}(\text{graphite}) + 2\text{Cl}_2(\text{g})$	+176 +135	+285 +235	Higher temperatures (> 619 K) Higher temperatures (> 574 K)
4	$2\text{H}_2\text{O}(\ell) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}_2(\ell)$ $3\text{O}_2(\text{g}) \longrightarrow 2\text{O}_3(\text{g})$	+196 +285	-126 -137	Nonspontaneous, all temperatures Nonspontaneous, all temperatures

EXAMPLE 15-22 Temperature Range of Spontaneity

Mercury(II) sulfide is a dark red mineral called cinnabar. Metallic mercury is obtained by roasting the sulfide in a limited amount of air. Estimate the temperature range in which the reaction is product-favored.



Plan

We evaluate ΔH_{rxn}^0 and ΔS_{rxn}^0 and assume that these values are independent of temperature. Each of these values allows us to assess its contribution to spontaneity.

Solution

From Appendix K:

	HgS(s)	O ₂	Hg(l)	SO ₂ (g)
ΔH_f° , kJ/mol:	-58.2	0	0	-296.8
S° , J/mol · K:	82.4	205.0	76.0	248.1

$$\Delta H_{\text{rxn}}^\circ = \Delta H_{\text{f Hg(l)}}^\circ + \Delta H_{\text{f SO}_2(\text{g})}^\circ - [\Delta H_{\text{f HgS(s)}}^\circ + \Delta H_{\text{f O}_2(\text{g})}^\circ]$$

$$= 0 - 296.8 - [-58.2 + 0] = -238.6 \text{ kJ/mol}$$

$$\Delta S_{\text{rxn}}^\circ = S_{\text{Hg(l)}}^\circ + S_{\text{SO}_2(\text{g})}^\circ - [S_{\text{HgS(s)}}^\circ + S_{\text{O}_2(\text{g})}^\circ]$$

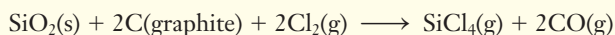
$$= 76.02 + 248.1 - [82.4 + 205.0] = +36.7 \text{ J/mol} \cdot \text{K}$$

When $\Delta H_{\text{rxn}}^\circ$ is negative (favorable to spontaneity) and $\Delta S_{\text{rxn}}^\circ$ is positive (favorable to spontaneity), the reaction must be spontaneous (product-favored) at all temperatures; no further calculation is necessary. The reverse reaction is, therefore, nonspontaneous at all temperatures.

The fact that a reaction is spontaneous at all temperatures does not mean that the reaction occurs rapidly enough to be useful at all temperatures. As a matter of fact, Hg(l) can be obtained from HgS(s) by this reaction at a reasonable rate only at high temperatures.

EXAMPLE 15-23 Temperature Range of Spontaneity

Estimate the temperature range for which the following reaction is product-favored.

**Plan**

When we proceed as in Example 15-22, we find that $\Delta S_{\text{rxn}}^\circ$ is favorable to spontaneity, whereas $\Delta H_{\text{rxn}}^\circ$ is unfavorable. Thus, we know that the reaction becomes product-favored *above* some temperature. We can set ΔG° equal to zero in the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and solve for the temperature at which the system is *at equilibrium*. This will represent the temperature above which the reaction would be product-favored.

Solution

From Appendix K:

	SiO ₂ (s)	C(graphite)	Cl ₂ (g)	SiCl ₄ (g)	CO(g)
ΔH_f° , kJ/mol:	-910.9	0	0	-657.0	-110.5
S° , J/mol · K:	41.84	5.740	223.0	330.6	197.6

$$\Delta H_{\text{rxn}}^\circ = [\Delta H_{\text{f SiCl}_4(\text{g})}^\circ + 2\Delta H_{\text{f CO}(\text{g})}^\circ] - [\Delta H_{\text{f SiO}_2(\text{s})}^\circ + 2\Delta H_{\text{f C}(\text{graphite})}^\circ + 2\Delta H_{\text{f Cl}_2(\text{g})}^\circ]$$

$$= [(-657.0) + 2(-110.5)] - [(-910.9) + 2(0) + 2(0)]$$

$$= +32.9 \text{ kJ/mol (unfavorable to spontaneity)}$$

$$\Delta S_{\text{rxn}}^\circ = \Delta S_{\text{SiCl}_4(\text{g})}^\circ + 2\Delta S_{\text{CO}(\text{g})}^\circ - [\Delta S_{\text{SiO}_2(\text{s})}^\circ + 2\Delta S_{\text{C}(\text{graphite})}^\circ + 2\Delta S_{\text{Cl}_2(\text{g})}^\circ]$$

$$= [330.6 + 2(197.6)] - [41.84 + 2(5.740) + 2(223.0)]$$

$$= 226.5 \text{ J/mol} \cdot \text{K} = 0.2265 \text{ kJ/mol} \cdot \text{K (favorable to spontaneity)}$$



Charles D. Winters

Heating red HgS in air produces liquid Hg. Gaseous SO₂ escapes. Cinnabar, an important ore of mercury, contains HgS.

STOP & THINK

When ΔH° and ΔS° are both *favorable*, we know without further calculation that ΔG° must be *negative* and the reaction must be *spontaneous (product-favored)* at all temperatures. When ΔH° and ΔS° are both *unfavorable*, we know without further calculation that ΔG° must be *positive* and the reaction must be *nonspontaneous (reactant-favored)* at all temperatures.

At the temperature at which $\Delta G^0 = 0$, neither the forward nor the reverse reaction is favored and the system is at equilibrium. Let's find this temperature.

$$0 = \Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta H^0 = T\Delta S^0$$

$$T = \frac{\Delta H^0}{\Delta S^0} = \frac{+32.9 \text{ kJ/mol}}{+0.2265 \text{ kJ/mol} \cdot \text{K}} = 145 \text{ K}$$

At temperatures above 145 K, the $T\Delta S^0$ term would be greater ($-T\Delta S^0$ would be more negative) than the ΔH^0 term, which would make ΔG^0 negative; so the reaction would be spontaneous (produced-favored) above 145 K. At temperatures below 145 K, the $T\Delta S^0$ term would be smaller than the ΔH^0 term, which would make ΔG^0 positive; so the reaction would be nonspontaneous below 145 K.

However, 145 K (-128°C) is a very low temperature. For all practical purposes, the reaction is product-favored at all but very low temperatures. In practice, it is carried out at 800°C to 1000°C because of the greater reaction rate at these higher temperatures. This gives a useful and economical rate of production of SiCl_4 , an important industrial chemical.

You should now work Exercises 116 and 120.

KEY TERMS

Absolute entropy (of a substance) The entropy of a substance relative to its entropy in a perfectly ordered crystalline form at 0 K (where its entropy is zero).

Bomb calorimeter A device used to measure the heat transfer between system and surroundings at constant volume.

Bond energy The amount of energy necessary to break one mole of bonds in a gaseous substance to form gaseous products at the same temperature and pressure.

Calorimeter A device used to measure the heat transfer that accompanies a physical or chemical change.

Dispersal of energy The degree to which the total energy of a system can be distributed among its particles.

Dispersal of matter The degree to which the particles of a sample can be distributed in space; also known as *disorder*.

Endothermic process A process that absorbs heat.

Enthalpy change, ΔH The quantity of heat transferred into or out of a system as it undergoes a chemical or physical change at constant temperature and pressure.

Entropy (S) A thermodynamic state function that measures the dispersal of energy and the dispersal of matter (disorder) of a system.

Equilibrium A state of dynamic balance in which the rates of forward and reverse processes (reactions) are equal; the state of a system when neither the forward nor the reverse process is thermodynamically favored.

Exothermic process A process that gives off (releases) heat.

First Law of Thermodynamics The total amount of energy in the universe is constant (also known as the Law of Conservation of Energy); energy is neither created nor destroyed in ordinary chemical reactions and physical changes.

Gibbs free energy (G) The thermodynamic state function of a system that indicates the amount of energy available for the system to do useful work at constant T and P . It is defined as $G = H - TS$; also known as *free energy*.

Heat of formation See *Standard molar enthalpy of formation*.

Hess's Law of Heat Summation The enthalpy change for a reaction is the same whether it occurs in one step or a series of steps.

Internal energy (E) All forms of energy associated with a specific amount of a substance.

Kinetic energy The energy of motion. The kinetic energy of an object is equal to one half its mass times the square of its velocity.

Law of Conservation of Energy Energy cannot be created or destroyed in a chemical reaction or in a physical change; it may be changed from one form to another; see *First Law of Thermodynamics*.

Mole of reaction (mol rxn) The amount of reaction that corresponds to the number of moles of each substance shown in the balanced equation.

Nonspontaneous change A change for which the collection of reactants is more stable than the collection of products under the given conditions; also known as *reactant-favored change*.

Potential energy The energy that a system or object possesses by virtue of its position or composition.

Pressure-volume work Work done by a gas when it expands against an external pressure, or work done on a system as gases are compressed or consumed in the presence of an external pressure.

Product-favored change See *Spontaneous change*.

Reactant-favored change See *Nonspontaneous change*.

Second Law of Thermodynamics The universe tends toward a state of greater disorder in spontaneous processes.

Spontaneous change A change for which the collection of products is more stable than the collection of reactants under the given conditions; also known as *product-favored change*.

Standard enthalpy change (ΔH^0) The enthalpy change in which the number of moles of reactants specified in the balanced chemical equation, all at standard states, is converted completely to the specified number of moles of products, all at standard states.

Standard entropy change (ΔS°) The entropy change in which the number of moles of reactants specified in the balanced chemical equation, all at standard states, is converted completely to the specified number of moles of products, all at standard states.

Standard Gibbs free energy change (ΔG°) The indicator of spontaneity of a process at constant T and P . If ΔG° is negative, the process is product-favored (spontaneous); if ΔG° is positive, the reverse process is reactant-favored (nonspontaneous).

Standard molar enthalpy of formation (ΔH_f°) (of a substance) The enthalpy change for the formation of one mole of a substance in a specified state from its elements in their standard states; also known as *standard molar heat of formation* or just *heat of formation*.

Standard molar heat of formation See *Standard molar enthalpy of formation*.

Standard molar entropy (S°) (of a substance) The absolute entropy of a substance in its standard state at 298 K.

Standard state (of a substance) See *Thermodynamic standard state of a substance*.

State function A variable that defines the state of a system; a function that is independent of the pathway by which a process occurs.

Surroundings Everything in the environment of the system.

System The substances of interest in a process; the part of the universe under investigation.

Thermochemical equation A balanced chemical equation together with a designation of the corresponding value of ΔH_{rxn} . Sometimes used with changes in other thermodynamic quantities.

Thermochemistry The observation, measurement, and prediction of energy changes for both physical changes and chemical reactions.

Thermodynamics The study of the energy transfers accompanying physical and chemical processes.

Thermodynamic state of a system A set of conditions that completely specifies all of the properties of the system.

Thermodynamic standard state of a substance The most stable state of the substance at one atmosphere pressure and at some specific temperature (25°C unless otherwise specified); also known as *standard state (of a substance)*.

Third Law of Thermodynamics The entropy of a hypothetical pure, perfect, crystalline substance at absolute zero temperature is zero.

Universe The system plus the surroundings.

Work The application of a force through a distance; for physical changes or chemical reactions at constant external pressure, the work done on the system is $-P\Delta V$; for chemical reactions that involve gases, the work done on the system can be expressed as $-(\Delta n)RT$.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

General Concepts

- State precisely the meaning of each of the following terms. You may need to review Chapter 1 to refresh your memory concerning terms introduced there. (a) energy; (b) kinetic energy; (c) potential energy; (d) joule.
- State precisely the meaning of each of the following terms. You may need to review Chapter 1 to refresh your memory about terms introduced there. (a) heat; (b) temperature; (c) system; (d) surroundings; (e) thermodynamic state of system; (f) work.
- (a) Give an example of the conversion of heat into work. (b) Give an example of the conversion of work into heat.
- (a) Give an example of heat being given off by the system. (b) Give an example of work being done on the system.
- (a) Give an example of heat being added to the system. (b) Give an example of work being done by the system.
- Distinguish between endothermic and exothermic processes. If we know that a reaction is endothermic in one direction, what can be said about the reaction in the reverse direction?
- According to the First Law of Thermodynamics, the total amount of energy in the universe is constant. Why, then, do we say that we are experiencing a declining supply of energy?

- Use the First Law of Thermodynamics to describe what occurs when an incandescent light is turned on.
- Define enthalpy and give an example of a reaction that has a negative enthalpy change.
- Which of the following are examples of state functions? (a) your bank balance; (b) the mass of a candy bar; (c) your weight; (d) the heat lost by perspiration during a climb up a mountain along a fixed path.
- What is a state function? Would Hess's Law be a law if enthalpy were not a state function?

Enthalpy and Changes in Enthalpy

- (a) Distinguish between ΔH and ΔH° for a reaction. (b) Distinguish between $\Delta H_{\text{rxn}}^\circ$ and ΔH_f° .
- A reaction is characterized by $\Delta H_{\text{rxn}} = +450 \text{ kJ/mol}$. Does the reaction mixture absorb heat from the surroundings or release heat to them?
- For each of the following reactions, (a) does the enthalpy increase or decrease; (b) is $H_{\text{reactants}} > H_{\text{products}}$ or is $H_{\text{products}} > H_{\text{reactants}}$; (c) is ΔH positive or negative?
(i) $\text{Al}_2\text{O}_3(\text{s}) \longrightarrow 2\text{Al}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g})$ (endothermic)
(ii) $\text{Sn}(\text{s}) + \text{Cl}_2(\text{g}) \longrightarrow \text{SnCl}_2(\text{s})$ (exothermic)

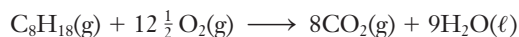
● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

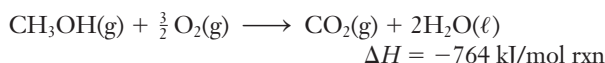
Unless otherwise noted, all content on this page is © Cengage Learning.

15. (a) The combustion of 0.0222 g of isooctane vapor, $\text{C}_8\text{H}_{18}(\text{g})$, at constant pressure raises the temperature of a calorimeter 0.400°C . The heat capacity of the calorimeter and water combined is $2.48 \text{ kJ}/^\circ\text{C}$. Find the molar heat of combustion of gaseous isooctane.



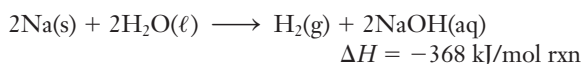
(b) How many grams of $\text{C}_8\text{H}_{18}(\text{g})$ must be burned to obtain 495 kJ of heat energy?

16. Methanol, CH_3OH , is an efficient fuel with a high octane rating.



(a) Find the heat evolved when 115.0 g $\text{CH}_3\text{OH}(\text{g})$ burns in excess oxygen. (b) What mass of O_2 is consumed when 925 kJ of heat is given off?

17. How much heat is liberated when 0.113 mole of sodium reacts with excess water according to the following equation?

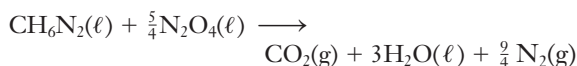


18. What is ΔH for the reaction

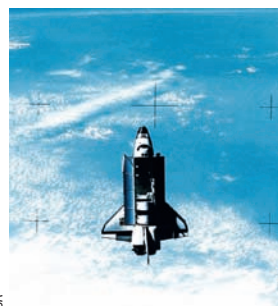


if 5.95 kJ must be supplied to convert 13.43 g lead(II) oxide to lead?

19. From the data in Appendix K, determine the form that represents the standard state for each of the following elements: iodine, oxygen, sulfur.
20. Why is the standard molar enthalpy of formation, ΔH_f° , for liquid water different than ΔH_f° for water vapor, both at 25°C ? Which formation reaction is more exothermic? Does your answer indicate that $\text{H}_2\text{O}(\ell)$ is at a higher or lower enthalpy than $\text{H}_2\text{O}(\text{g})$?
21. Methylhydrazine is burned with dinitrogen tetroxide in the attitude-control engines of the space shuttles.



The two substances ignite instantly on contact, producing a flame temperature of 3000. K. The energy liberated per 0.100 g of CH_6N_2 at constant atmospheric pressure after the products are cooled back to 25°C is 750. J. (a) Find ΔH for the reaction as written. (b) How many kilojoules are liberated when 87.5 g of N_2 is produced?



NASA

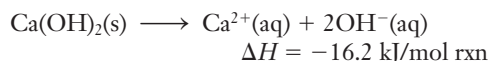
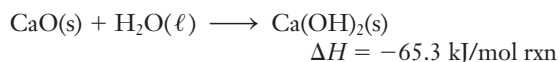
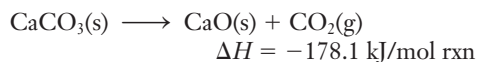
A space shuttle

22. Which is more exothermic, the combustion of one mole of methane to form $\text{CO}_2(\text{g})$ and liquid water or the combustion of one mole of methane to form $\text{CO}_2(\text{g})$ and steam? Why? (No calculations are necessary.)
23. Which is more exothermic, the combustion of one mole of gaseous benzene, C_6H_6 , or the combustion of one mole of liquid benzene? Why? (No calculations are necessary.)

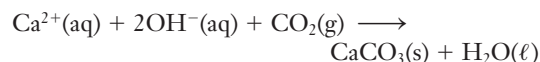
Thermochemical Equations, ΔH_f° , and Hess's Law

24. Explain the meaning of the phrase "thermodynamic standard state of a substance."
25. Explain the meaning of the phrase "standard molar enthalpy of formation." Give an example.
26. From the data in Appendix K, determine the form that represents the standard state for each of the following elements: (a) chlorine; (b) chromium; (c) bromine; (d) iodine; (e) sulfur; (f) nitrogen.
27. From the data in Appendix K, determine the form that represents the standard state for each of the following elements: (a) oxygen; (b) carbon; (c) phosphorus; (d) rubidium; (e) mercury; (f) tin.
28. Write the balanced chemical equation whose $\Delta H_{\text{rxn}}^\circ$ value is equal to ΔH_f° for each of the following substances: (a) calcium hydroxide, $\text{Ca}(\text{OH})_2(\text{s})$; (b) benzene, $\text{C}_6\text{H}_6(\ell)$; (c) sodium bicarbonate, $\text{NaHCO}_3(\text{s})$; (d) calcium fluoride, $\text{CaF}_2(\text{s})$; (e) phosphine, $\text{PH}_3(\text{g})$; (f) propane, $\text{C}_3\text{H}_8(\text{g})$; (g) atomic sulfur, $\text{S}(\text{g})$; (h) water, $\text{H}_2\text{O}(\ell)$.
29. Write the balanced chemical equation for the formation of one mole of each of the following substances from its elements in the standard state (the equation whose $\Delta H_{\text{rxn}}^\circ$ value is equal to ΔH_f° for the substance): hydrogen peroxide [$\text{H}_2\text{O}_2(\ell)$], calcium fluoride [$\text{CaF}_2(\text{s})$], ruthenium(III) hydroxide [$\text{Ru}(\text{OH})_3(\text{s})$].
30. We burn 3.47 g of lithium in excess oxygen at constant atmospheric pressure to form Li_2O . Then we bring the reaction mixture back to 25°C . In this process 146 kJ of heat is given off. What is the standard molar enthalpy of formation of Li_2O ?
31. We burn 7.20 g of magnesium in excess nitrogen at constant atmospheric pressure to form Mg_3N_2 . Then we bring the reaction mixture back to 25°C . In this process 68.35 kJ of heat is given off. What is the standard molar enthalpy of formation of Mg_3N_2 ?
32. From the following enthalpies of reaction,
- $$4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\ell) + 2\text{Cl}_2(\text{g})$$
- $$\Delta H = -202.4 \text{ kJ/mol rxn}$$
- $$\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{F}_2(\text{g}) \longrightarrow \text{HF}(\ell)$$
- $$\Delta H = -600.0 \text{ kJ/mol rxn}$$
- $$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell)$$
- $$\Delta H = -285.8 \text{ kJ/mol rxn}$$
- find ΔH_{rxn} for $2\text{HCl}(\text{g}) + \text{F}_2(\text{g}) \longrightarrow 2\text{HF}(\ell) + \text{Cl}_2(\text{g})$.

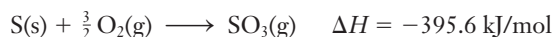
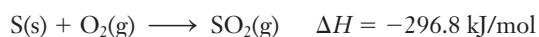
33. From the following enthalpies of reaction,



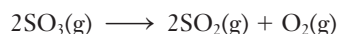
calculate ΔH_{rxn} for



34. Given that



determine the enthalpy change for the decomposition reaction

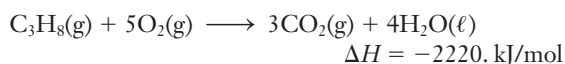
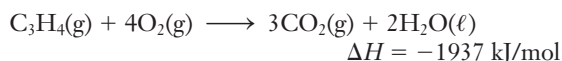
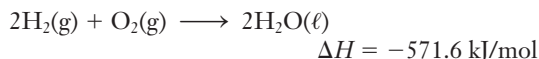


35. Evaluate ΔH_{rxn}^0 for the reaction below at 25°C , using the heats of formation.

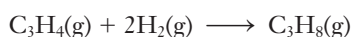


$$\Delta H_f^0, \text{ kJ/mol:} \quad -1118 \quad -110.5 \quad -272 \quad -393.5$$

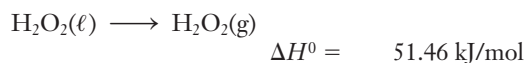
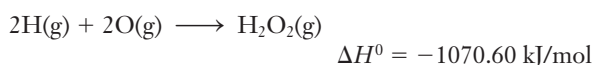
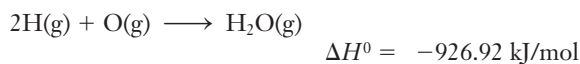
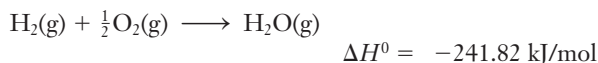
36. Given that



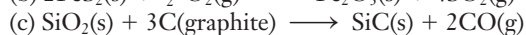
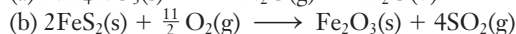
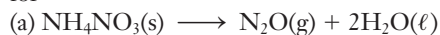
determine the heat of the hydrogenation reaction



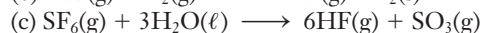
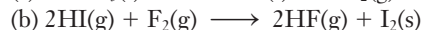
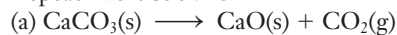
37. Determine the heat of formation of liquid hydrogen peroxide at 25°C from the following thermochemical equations.



38. Use data in Appendix K to find the enthalpy of reaction for



39. Repeat Exercise 38 for



40. The internal combustion engine uses heat produced during the burning of a fuel. Propane, $\text{C}_3\text{H}_8(\text{g})$, is sometimes used as the fuel. Gasoline is the most commonly used fuel. Assume that the gasoline is pure octane, $\text{C}_8\text{H}_{18}(\ell)$, and the fuel and oxygen are completely converted into $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. For each of these fuels, determine the heat released per gram of fuel burned.

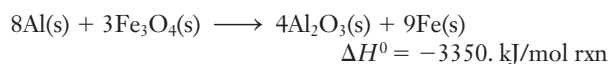
41. Write the balanced equation for the complete combustion (in excess O_2) of kerosene. Assume that kerosene is $\text{C}_{10}\text{H}_{22}(\ell)$ and that the products are $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$. Calculate ΔH_{rxn}^0 at 25°C for this reaction.

$$\Delta H_f^0 \text{ C}_{10}\text{H}_{22}(\ell) = -249.6 \text{ kJ/mol}$$

$$\Delta H_f^0 \text{ CO}_2(\text{g}) = -393.5 \text{ kJ/mol}$$

$$\Delta H_f^0 \text{ H}_2\text{O}(\ell) = -285.8 \text{ kJ/mol}$$

42. The thermite reaction, used for welding iron, is the reaction of Fe_3O_4 with Al.



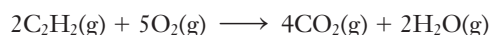
Because this large amount of heat cannot be rapidly dissipated to the surroundings, the reacting mass may reach temperatures near $3000.^\circ\text{C}$. How much heat is released by the reaction of 27.6 g of Al with 69.12 g of Fe_3O_4 ?



Charles D. Winters

The thermite reaction

43. When a welder uses an acetylene torch, the combustion of acetylene liberates the intense heat needed for welding metals together. The equation for this combustion reaction is



The heat of combustion of acetylene is -1255.5 kJ/mol of C_2H_2 . How much heat is liberated when 1.731 kg of C_2H_2 is burned?



Molecular Reasoning exercises

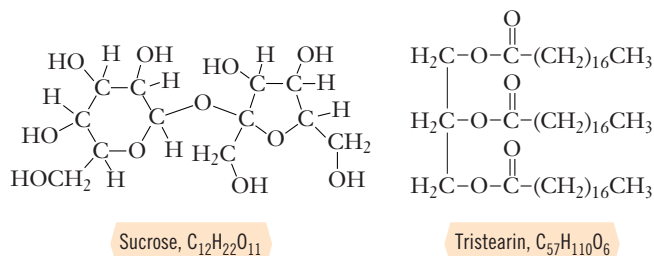


More Challenging exercises

Blue-Numbered

exercises solved in Student Solutions Manual

44. ▲ Write balanced equations for the oxidation of sucrose (a carbohydrate) and tristearin (a fat). Assume that each reacts with $O_2(g)$, producing $CO_2(g)$ and $H_2O(g)$.



Use tabulated bond energies to estimate ΔH_{rxn}^0 for each reaction in kJ/mol (ignoring phase changes). Convert to kJ/g and kcal/g. Which has the greater energy density?

45. Natural gas is mainly methane, $CH_4(g)$. Assume that gasoline is octane, $C_8H_{18}(l)$, and that kerosene is $C_{10}H_{22}(l)$. (a) Write the balanced equations for the combustion of each of these three hydrocarbons in excess O_2 . The products are $CO_2(g)$ and $H_2O(l)$. (b) Calculate at $25^\circ C$ for each combustion reaction. ΔH_f^0 for $C_{10}H_{22}$ is -300.9 kJ/mol. (c) When burned at standard conditions, which of these three fuels would produce the most heat per mole? (d) When burned at standard conditions, which of the three would produce the most heat per gram?

Bond Energies

46. (a) How is the heat released or absorbed in a *gas phase reaction* related to bond energies of products and reactants? (b) Hess's Law states that

$$\Delta H_{rxn}^0 = \sum n \Delta H_f^0 \text{ products} - \sum n \Delta H_f^0 \text{ reactants}$$

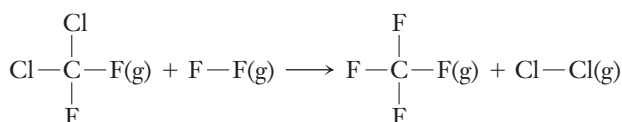
The relationship between ΔH_{rxn}^0 and bond energies for a *gas phase reaction* is

$$\Delta H_{rxn}^0 = \sum \text{bond energies}_{\text{reactants}} - \sum \text{bond energies}_{\text{products}}$$

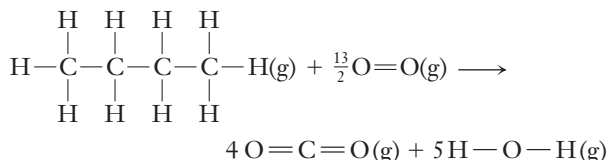
It is *not* true, in general, that ΔH_f^0 for a substance is equal to the negative of the sum of the bond energies of the substance. Why?

47. (a) Suggest a reason for the fact that different amounts of energy are required for the successive removal of the three hydrogen atoms of an ammonia molecule, even though all N—H bonds in ammonia are equivalent. (b) Suggest why the N—H bonds in different compounds such as ammonia, NH_3 ; methylamine, CH_3NH_2 ; and ethylamine, $C_2H_5NH_2$, have slightly different bond energies.
48. Use tabulated bond energies to estimate the enthalpy of reaction for each of the following gas phase reactions.
- (a) $H_2C=CH_2 + Br_2 \longrightarrow BrH_2C-CH_2Br$
 (b) $H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$
49. Use tabulated bond energies to estimate the enthalpy of reaction for each of the following gas phase reactions.
- (a) $N_2 + 3H_2 \longrightarrow 2NH_3$
 (b) $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$
 (c) $CO + H_2O \longrightarrow CO_2 + H_2$

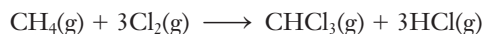
50. Use the bond energies listed in Table 15-2 to estimate the heat of reaction for



51. Estimate ΔH for the burning of one mole of butane, using the bond energies listed in Tables 15-2 and 15-3.



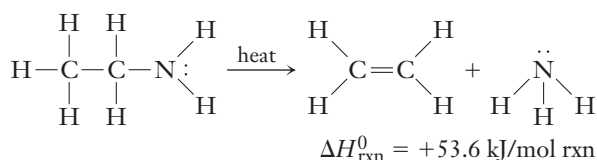
52. (a) Use the bond energies listed in Table 15-2 to estimate the heats of formation of $HCl(g)$ and $HF(g)$. (b) Compare your answers to the standard heats of formation in Appendix K.
53. (a) Use the bond energies listed in Table 15-2 to estimate the heats of formation of $H_2O(g)$ and $O_3(g)$. (b) Compare your answers to the standard heats of formation in Appendix K.
54. Using data in Appendix K, calculate the average P—Cl bond energy in $PCl_3(g)$.
55. Using data in Appendix K, calculate the average P—H bond energy in $PH_3(g)$.
56. Using data in Appendix K, calculate the average P—Cl bond energy in $PCl_5(g)$. Compare your answer with the value calculated in Exercise 54.
57. ● ▲ Methane undergoes several different exothermic reactions with gaseous chlorine. One of these forms chloroform, $CHCl_3(g)$.



$$\Delta H_{rxn}^0 = -305.2 \text{ kJ/mol rxn}$$

Average bond energies per mole of bonds are: C—H = 413 kJ; Cl—Cl = 242 kJ; H—Cl = 432 kJ. Use these to calculate the average C—Cl bond energy in chloroform. Compare this with the value in Table 15-2.

58. ▲ Ethylamine undergoes an endothermic gas phase dissociation to produce ethylene (or ethene) and ammonia.



The following average bond energies per mole of bonds are given: C—H = 413 kJ; C—C = 346 kJ; C=C = 602 kJ; N—H = 391 kJ. Calculate the C—N bond energy in ethylamine. Compare this with the value in Table 15-2.

Calorimetry

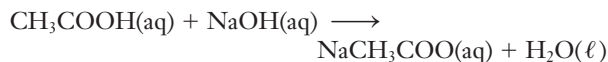
59. ● What is a coffee-cup calorimeter? How do coffee-cup calorimeters give us useful information?

60. A calorimeter contained 75.0 g of water at 16.95°C. A 93.3-g sample of iron at 65.58°C was placed in it, giving a final temperature of 19.68°C for the system. Calculate the heat capacity of the calorimeter. Specific heats are 4.184 J/g · °C for H₂O and 0.444 J/g · °C for Fe.
61. ▲ A student wishes to determine the heat capacity of a coffee-cup calorimeter. After she mixes 100.0 g of water at 58.5°C with 100.0 g of water, already in the calorimeter, at 22.8°C, the final temperature of the water is 39.7°C. (a) Calculate the heat capacity of the calorimeter in J/°C. Use 4.184 J/g · °C as the specific heat of water. (b) Why is it more useful to express the value in J/°C rather than units of J/(g calorimeter · °C)?
62. A coffee-cup calorimeter is used to determine the specific heat of a metallic sample. The calorimeter is filled with 50.0 mL of water at 25.0°C (density = 0.997 g/mL). A 36.5-gram sample of the metallic material is taken from water boiling at 100.0°C and placed in the calorimeter. The equilibrium temperature of the water and sample is 32.5°C. The calorimeter constant is known to be 1.87 J/°C. Calculate the specific heat of the metallic material.
63. A 5.1-gram piece of gold jewelry is removed from water at 100.0°C and placed in a coffee-cup calorimeter containing 16.9 g of water at 22.5°C. The equilibrium temperature of the water and jewelry is 23.2°C. The calorimeter constant is known from calibration experiments to be 1.54 J/°C. What is the specific heat of this piece of jewelry? The specific heat of pure gold is 0.129 J/g · °C. Is the jewelry pure gold?
64. A coffee-cup calorimeter having a heat capacity of 472 J/°C is used to measure the heat evolved when the following aqueous solutions, both initially at 22.6°C, are mixed: 100. g of solution containing 6.62 g of lead(II) nitrate, Pb(NO₃)₂, and 100. g of solution containing 6.00 g of sodium iodide, NaI. The final temperature is 24.2°C. Assume that the specific heat of the mixture is the same as that for water, 4.184 J/g · °C. The reaction is



(a) Calculate the heat evolved in the reaction. (b) Calculate the ΔH for the reaction under the conditions of the experiment.

65. A coffee-cup calorimeter is used to determine the heat of reaction for the acid–base neutralization

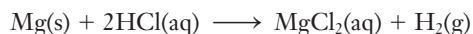


When we add 20.00 mL of 0.625 M NaOH at 21.400°C to 30.00 mL of 0.500 M CH₃COOH already in the calorimeter at the same temperature, the resulting temperature is observed to be 24.347°C. The heat capacity of the calorimeter has previously been determined to be 27.8 J/°C. Assume that the specific heat of the mixture is the same as that of water, 4.184 J/g · °C, and that the density of the mixture is 1.02 g/mL. (a) Calculate the amount of heat given off in the reaction. (b) Determine ΔH for the reaction under the conditions of the experiment.

66. In a bomb calorimeter compartment surrounded by 945 g of water, the combustion of 1.048 g of benzene, C₆H₆(ℓ), raised

the temperature of the water from 23.640°C to 32.692°C. The heat capacity of the calorimeter is 891 J/°C. (a) Write the balanced equation for the combustion reaction, assuming that CO₂(g) and H₂O(ℓ) are the only products. (b) Use the calorimetric data to calculate ΔE for the combustion of benzene in kJ/g and in kJ/mol.

67. A 2.00-g sample of hydrazine, N₂H₄, is burned in a bomb calorimeter that contains 6.40 × 10³ g of H₂O, and the temperature increases from 25.00°C to 26.17°C. The heat capacity of the calorimeter is 3.76 kJ/°C. Calculate ΔE for the combustion of N₂H₄ in kJ/g and in kJ/mol.
68. ▲ A strip of magnesium metal having a mass of 1.22 g dissolves in 100. mL of 6.02 M HCl, which has a specific gravity of 1.10. The hydrochloric acid is initially at 23.0°C, and the resulting solution reaches a final temperature of 45.5°C. The heat capacity of the calorimeter in which the reaction occurs is 562 J/°C. Calculate ΔH for the reaction under the conditions of the experiment, assuming the specific heat of the final solution is the same as that for water, 4.184 J/g · °C.



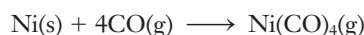
69. When 3.16 g of salicylic acid, C₇H₆O₃, is burned in a bomb calorimeter containing 5.00 kg of water originally at 23.00°C, 69.3 kJ of heat is evolved. The calorimeter constant is 3255 J/°C. Calculate the final temperature.
70. A 6.620-g sample of decane, C₁₀H₂₂(ℓ), was burned in a bomb calorimeter whose heat capacity had been determined to be 2.45 kJ/°C. The temperature of 1250.0 g of water rose from 24.6°C to 26.4°C. Calculate ΔE for the reaction in joules per gram of decane and in kilojoules per mole of decane. The specific heat of water is 4.184 J/g · °C.
71. A nutritionist determines the caloric value of a 10.00-g sample of beef fat by burning it in a bomb calorimeter. The calorimeter held 2.500 kg of water, the heat capacity of the bomb is 1.360 kJ/°C, and the temperature of the calorimeter increased from 25.0°C to 56.9°C. (a) Calculate the number of joules released per gram of beef fat. (b) One nutritional Calorie is 1 kcal or 4184 joules. What is the dietary, caloric value of beef fat, in nutritional Calories per gram?

Internal Energy and Changes in Internal Energy

72. (a) What are the sign conventions for q , the amount of heat added to or removed from a system? (b) What are the sign conventions for w , the amount of work done on or by a system?
73. What happens to ΔE for a system during a process in which (a) $q < 0$ and $w < 0$, (b) $q = 0$ and $w > 0$, and (c) $q > 0$ and $w < 0$.
74. Ammonium nitrate, commonly used as a fertilizer, decomposes explosively:
- $$2\text{NH}_4\text{NO}_3(\text{s}) \longrightarrow 2\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$$
- (This reaction has been responsible for several major explosions.) For this reaction:
- (a) Is work (w) positive, negative, or 0?
- (b) If $w < 0$, is work done on the system or by the system?



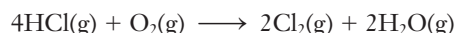
75. A system performs 720. L · atm of pressure–volume work (1 L · atm = 101.325 J) on its surroundings and absorbs 5750. J of heat from its surroundings. What is the change in internal energy of the system?
76. A system receives 96 J of electrical work, performs 257 J of pressure–volume work, and releases 175 J of heat. What is the change in internal energy of the system?
77. For each of the following chemical and physical changes carried out at constant pressure, state whether work is done by the system on the surroundings or by the surroundings on the system, or whether the amount of work is negligible.
- $\text{C}_6\text{H}_6(\ell) \longrightarrow \text{C}_6\text{H}_6(\text{g})$
 - $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \longrightarrow \text{NH}_3(\text{g})$
 - $\text{SiO}_2(\text{s}) + 3\text{C}(\text{s}) \longrightarrow \text{SiC}(\text{s}) + 2\text{CO}(\text{g})$
78. Repeat Exercise 77 for
- $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{SO}_3(\text{g})$
 - $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 - $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell) + \text{CaCO}_3(\text{s}) \longrightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{HCO}_3^{-}(\text{aq})$
79. Assuming that the gases are ideal, calculate the amount of work done (in joules) in each of the following reactions. In each case, is the work done *on* or *by* the system? (a) A reaction in the Mond process for purifying nickel that involves formation of the gas nickel(0) tetracarbonyl at 50–100°C. Assume one mole of nickel is used and a constant temperature of 75°C is maintained.



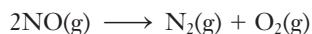
- (b) The conversion of one mole of brown nitrogen dioxide into colorless dinitrogen tetroxide at 8.0°C.



80. Assuming that the gases are ideal, calculate the amount of work done (in joules) in each of the following reactions. In each case, is the work done *on* or *by* the system? (a) The oxidation of one mole of HCl(g) at 200°C.



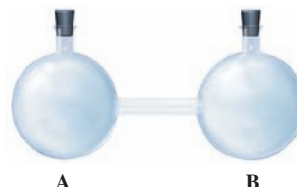
- (b) The decomposition of one mole of nitric oxide (an air pollutant) at 300.°C.



81. ▲ When an ideal gas expands at *constant temperature*, there is no change in molecular kinetic energy (kinetic energy is proportional to temperature), and there is no change in potential energy due to intermolecular attractions (these are zero for an ideal gas). Thus for the isothermal (constant temperature) expansion of an ideal gas, $\Delta E = 0$. Suppose we allow an ideal gas to expand isothermally from 2.50 L to 5.50 L in two steps: (a) against a constant external pressure of 3.50 atm until equilibrium is reached, then (b) against a constant external pressure of 2.50 atm until equilibrium is reached. Calculate q and w for this two-step expansion.

Entropy and Entropy Changes

82. ● A car uses gasoline as a fuel. Describe the burning of the fuel in terms of chemical and physical changes. Relate your answer to the Second Law of Thermodynamics.
83. State the Second Law of Thermodynamics. Why can't we use ΔS_{univ} directly as a measure of the spontaneity of a reaction?
84. State the Third Law of Thermodynamics. What does it mean?
85. Explain why ΔS may be referred to as a contributor to spontaneity.
86. Suppose you flip a coin. (a) What is the probability that it will come up heads? (b) What is the probability that it will come up heads two times in a row? (c) What is the probability that it will come up heads ten times in a row?
87. ● Consider two equal-sized flasks connected as shown in the figure.



- (a) Suppose you put one molecule inside. What is the probability that the molecule will be in flask A? What is the probability that it will be in flask B?
- (b) If you put 100 molecules into the two-flask system, what is the most likely distribution of molecules? Which distribution corresponds to the highest entropy?
- (c) Write a mathematical expression for the probability that all 100 molecules in part (b) will be in flask A. (You do not need to evaluate this expression.)
88. ● Suppose you have two identical red molecules labeled A and B, and two identical blue molecules labeled C and D. Draw a simple two-flask diagram as in the figure for Exercise 87, and then draw all possible arrangements of the four molecules in the two flasks.
- (a) How many different arrangements are possible?
- (b) How many of the arrangements have a mixture of unlike molecules in at least one of the flasks?
- (c) What is the probability that at least one of the flasks contains a mixture of unlike molecules?
- (d) What is the probability that the gases are not mixed (each flask contains only like molecules)?
89. ● For each process, tell whether the entropy change of the system is positive or negative. (a) Water vapor (the system) condenses as droplets on a cold windowpane. (b) Water boils. (c) A can of carbonated beverage loses its fizz. (Consider the beverage, but not the can, as the system. What happens to the entropy of the dissolved gas?)
90. ● For each process, tell whether the entropy change of the system is positive or negative. (a) A glassblower heats glass (the system) to its softening temperature.

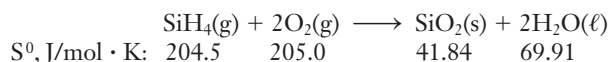
- (b) A teaspoon of sugar dissolves in a cup of coffee. (The system consists of both sugar and coffee.) (c) Calcium carbonate precipitates out of water in a cave to form stalactites and stalagmites. (Consider only the calcium carbonate to be the system.)
91. ● For each of the following processes, tell whether the entropy of the *universe* increases, decreases, or remains constant: (a) melting one mole of ice to water at 0.°C; (b) freezing one mole of water to ice at 0.°C; (c) freezing one mole of water to ice at -15°C; (d) freezing one mole of water to ice at 0.°C and then cooling it to -15°C.
92. ▲ In which of the following changes is there an increase in entropy?
 (a) the freezing of water
 (b) the condensation of steam
 (c) the sublimation of dry ice, solid CO₂
 (d) the separation of salts and pure water from seawater
93. ● When solid sodium chloride is cooled from 25°C to 0.°C, the entropy change is -4.4 J/mol · K. Is this an increase or decrease in randomness? Explain this entropy change in terms of what happens in the solid at the molecular level.
94. ● When a one-mole sample of argon gas at 0.°C is compressed to one half its original volume, the entropy change is -5.76 J/mol · K. Is this an increase or a decrease in dispersal of energy? Explain this entropy change in terms of what happens in the gas at the molecular level.
95. ● Which of the following processes are accompanied by an increase in entropy of the system? (No calculation is necessary.) (a) Dry ice, CO₂(s), sublimates at -78°C and then the resulting CO₂(g) is warmed to 0°C. (b) Water vapor forms snowflakes, H₂O(s). (c) Iodine sublimates, I₂(s) → I₂(g). (d) White silver sulfate, Ag₂SO₄, precipitates from a solution containing silver ions and sulfate ions. (e) A partition is removed to allow two gases to mix.
96. ● ▲ Which of the following processes are accompanied by an increase in entropy of the system? (No calculation is necessary.) (a) Solid NaCl is dissolved in water at room temperature. (b) A saturated solution of NaCl is cooled, causing some solid NaCl to precipitate. (c) Water freezes. (d) Carbon tetrachloride, CCl₄, evaporates. (e) The reaction PCl₃(g) → PCl₃(g) + Cl₂(g) occurs. (f) The reaction PCl₃(g) + Cl₂(g) → PCl₅(g) occurs.
97. ● For each pair, tell which would have the greater absolute entropy per mole (standard molar entropy) at the same temperature. Give the reasons for your choice.
 (a) NaCl(s) or CaO(s)
 (b) Cl₂(g) or P₄(g)
 (c) AsH₃(g) or Kr(g)
 (d) NH₄NO₃(s) or NH₄NO₃(aq)
 (e) Ga(s) or Ga(l)
98. ● For each pair, tell which would have the greater absolute entropy per mole (standard molar entropy) at the same temperature. Give the reasons for your choice.
 (a) NaF(s) or MgO(s)
 (b) Au(s) or Hg(l)
 (c) H₂O(g) or H₂S(g)
 (d) CH₃OH(l) or C₂H₅OH(l)
 (e) NaOH(s) or NaOH(aq)
99. ● (a) For which change would the entropy change by the greatest amount: (i) condensation of one mole of water vapor to make one mole of liquid water, or (ii) deposition of one mole of water vapor to make one mole of ice? (b) Would the entropy changes for the changes in (a) be positive or negative? Give reasons for your answer.
100. ● Without doing a calculation predict whether the entropy change will be positive or negative when each reaction occurs in the direction it is written.
 (a) C₃H₆(g) + H₂(g) → C₃H₈(g)
 (b) N₂(g) + 3H₂(g) → 2NH₃(g)
 (c) CaCO₃(s) → CaO(s) + CO₂(g)
 (d) Mg(s) + $\frac{1}{2}$ O₂(g) → MgO(s)
 (e) Ag⁺(aq) + Cl⁻(aq) → AgCl(s)
101. ● Without doing a calculation predict whether the entropy change will be positive or negative when each reaction occurs in the direction it is written.
 (a) CH₃OH(l) + $\frac{3}{2}$ O₂(g) → CO₂(g) + 2H₂O(g)
 (b) Br₂(l) + H₂(g) → 2HBr(g)
 (c) Na(s) + $\frac{1}{2}$ F₂(g) → NaF(s)
 (d) CO₂(g) + 2H₂(g) → CH₃OH(l)
 (e) NH₃(g) → N₂(g) + 3H₂(g)
102. ● ▲ Consider the boiling of a pure liquid at constant pressure. Is each of the following greater than, less than, or equal to zero? (a) ΔS_{sys}; (b) ΔH_{sys}; (c) ΔT_{sys}.
103. Use S⁰ data from Appendix K to calculate the value of ΔS⁰₂₉₈ for each of the following reactions. Compare the signs and magnitudes for these ΔS⁰₂₉₈ values and explain your observations.
 (a) 2NO(g) + H₂(g) → N₂O(g) + H₂O(g)
 (b) 2N₂O₅(g) → 4NO₂(g) + O₂(g)
 (c) NH₄NO₃(s) → N₂O(g) + 2H₂O(g)
104. Use S⁰ data from Appendix K to calculate the value of ΔS⁰₂₉₈ for each of the following reactions. Compare the signs and magnitudes for these ΔS⁰₂₉₈ values and explain your observations.
 (a) 4HCl(g) + O₂(g) → 2Cl₂(g) + 2H₂O(g)
 (b) PCl₃(g) + Cl₂(g) → PCl₅(g)
 (c) 2N₂O(g) → 2N₂(g) + O₂(g)

Gibbs Free Energy Changes and Spontaneity

105. ● (a) What are the two factors that favor spontaneity of a process? (b) What is Gibbs free energy? What is change in Gibbs free energy? (c) Most spontaneous reactions are exothermic, but some are not. Explain. (d) Explain how the signs and magnitudes of ΔH and ΔS are related to the spontaneity of a process.
106. Which of the following conditions would predict a process that is (a) always spontaneous, (b) always nonspontaneous, or (c) spontaneous or nonspontaneous depending on the temperature and magnitudes of ΔH and ΔS? (i) ΔH > 0, ΔS > 0; (ii) ΔH > 0, ΔS < 0; (iii) ΔH < 0, ΔS > 0; (iv) ΔH < 0, ΔS < 0
107. Calculate ΔG⁰ at 45°C for reactions for which
 (a) ΔH⁰ = 293 kJ; ΔS⁰ = -695 J/K.
 (b) ΔH⁰ = -1137 kJ; ΔS⁰ = 0.496 kJ/K.
 (c) ΔH⁰ = -86.6 kJ; ΔS⁰ = -382 J/K.



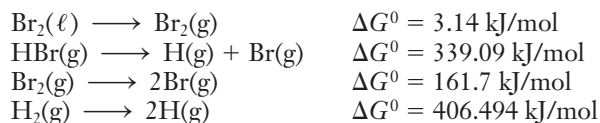
108. Evaluate ΔS° at 25°C and 1 atm for the reaction:



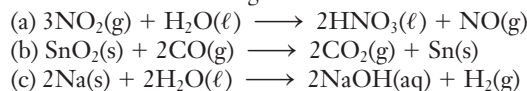
109. The standard Gibbs free energy of formation is -286.06 kJ/mol for $\text{NaI}(\text{s})$, -261.90 kJ/mol for $\text{Na}^+(\text{aq})$, and -51.57 kJ/mol for $\text{I}^-(\text{aq})$ at 25°C. Calculate ΔG° for the reaction



110. ▲ Use the following equations to find ΔG_f° for $\text{HBr}(\text{g})$ at 25°C.

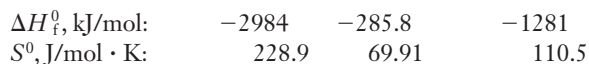
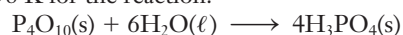


111. Use values of standard free energy of formation, ΔG_f° , from Appendix K to calculate the standard free energy change for each of the following reactions at 25°C and 1 atm.



112. Make the same calculations as in Exercise 111, using values of standard enthalpy of formation and absolute entropy instead of values of ΔG_f° .

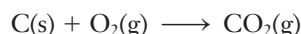
113. Calculate ΔG° at 298 K for the reaction:



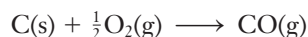
Temperature Range of Spontaneity

114. Are the following statements true or false? Justify your answers. (a) An exothermic reaction is always spontaneous. (b) If ΔH and ΔS are both positive, then ΔG will decrease when the temperature increases. (c) A reaction for which ΔS_{sys} is positive is spontaneous.

115. For the reaction



$\Delta H^\circ = -393.51 \text{ kJ/mol}$ and $\Delta S^\circ = 2.86 \text{ J/mol} \cdot \text{K}$ at 25°C. (a) Does this reaction become more or less favorable as the temperature increases? (b) For the reaction



$\Delta H^\circ = -110.52 \text{ kJ/mol}$ and $\Delta S^\circ = 89.36 \text{ J/mol} \cdot \text{K}$ at 25°C. Does this reaction become more or less favorable as the temperature increases? (c) Compare the temperature dependencies of these reactions.

116. (a) Calculate ΔH° , ΔG° , and ΔS° for the reaction

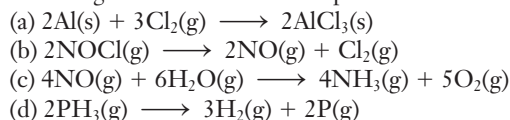


(b) Is there any temperature at which $\text{H}_2\text{O}_2(\ell)$ is stable at 1 atm?

117. When is it true that $\Delta S = \frac{\Delta H}{T}$?

118. ● Dissociation reactions are those in which molecules break apart. Why do high temperatures favor the spontaneity of most dissociation reactions?

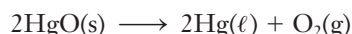
119. Estimate the temperature range over which each of the following standard reactions is spontaneous.



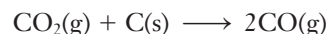
120. Estimate the temperature range over which each of the following standard reactions is spontaneous. (a) The reaction by which sulfuric acid droplets from polluted air convert water-insoluble limestone or marble (calcium carbonate) to slightly soluble calcium sulfate, which is slowly washed away by rain:



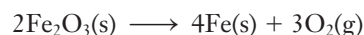
(b) The reaction by which Antoine Lavoisier achieved the first laboratory preparation of oxygen in the late eighteenth century: the thermal decomposition of the red-orange powder, mercury(II) oxide, to oxygen and the silvery liquid metal, mercury:



(c) The reaction of coke (carbon) with carbon dioxide to form the reducing agent, carbon monoxide, which is used to reduce some metal ores to metals:



(d) The reverse of the reaction by which iron rusts:



121. Estimate the normal boiling point of pentacarbonyliron(0), $\text{Fe}(\text{CO})_5$, at 1 atm pressure, using Appendix K.

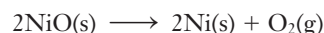
122. (a) Estimate the normal boiling point of water, at 1 atm pressure, using Appendix K. (b) Compare the temperature obtained with the known boiling point of water. Can you explain the discrepancy?

123. Sublimation and subsequent deposition onto a cold surface are a common method of purification of I_2 and other solids that sublime readily. Estimate the sublimation temperature (solid to vapor) of the dark violet solid iodine, I_2 , at 1 atm pressure, using the data of Appendix K.



Sublimation and deposition of I_2

124. Some metal oxides can be decomposed to the metal and oxygen under reasonable conditions. Is the decomposition of nickel(II) oxide product-favored at 25°C?



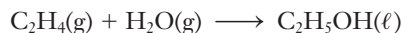
If not, can it become so if the temperature is raised? At what temperature does the reaction become product-favored?

125. Calculate ΔH^0 and ΔS^0 for the reaction of tin(IV) oxide with carbon.



- (a) Is the reaction spontaneous under standard conditions at 298 K?
 (b) Is the reaction predicted to be spontaneous at higher temperatures?

126. Calculate ΔS^0 system at 25°C for the reaction



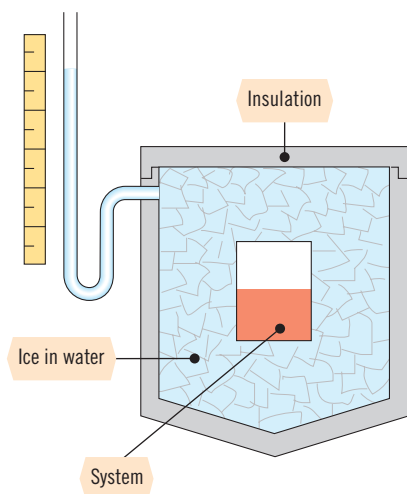
Can you tell from the result of this calculation whether this reaction is product-favored? If you cannot tell, what additional information do you need? Obtain that information and determine whether the reaction is product-favored.

Mixed Exercises

127. ▲ An ice calorimeter, shown below, can be used to measure the amount of heat released or absorbed by a reaction that is carried out at a constant temperature of 0°C. If heat is transferred from the system to the bath, some of the ice melts. A given mass of liquid water has a smaller volume than the same mass of ice, so the total volume of the ice and water mixture decreases. Measuring the volume decrease using the scale at the left indicates the amount of heat released by the reacting system. As long as some ice remains in the bath, the temperature remains at 0°C. In Example 15-2 we saw that the reaction

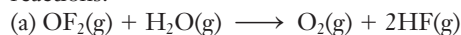


releases 846 J of heat at constant temperature and pressure when 50.0 mL of 0.400 M CuSO_4 solution and 50.0 mL of 0.600 M NaOH solution are allowed to react. (Because no gases are involved in the reaction, the volume change of the reaction mixture is negligible.) Calculate the change in volume of the ice and water mixture that would be observed if we carried out the same experiment in an ice calorimeter. The density of $\text{H}_2\text{O}(\ell)$ at 0°C is 0.99987 g/mL and that of ice is 0.917 g/mL. The heat of fusion of ice at 0°C is 334 J/g.



128. It is difficult to prepare many compounds directly from their elements, so ΔH_f^0 values for these compounds cannot be measured directly. For many organic compounds, it is easier to measure the standard enthalpy of combustion by reaction of the compound with excess $\text{O}_2(\text{g})$ to form $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\ell)$. From the following standard enthalpies of combustion at 25°C, determine ΔH_f^0 for the compound. (a) cyclohexane, $\text{C}_6\text{H}_{12}(\ell)$, a useful organic solvent: $\Delta H_{\text{combustion}}^0 = -3920$ kJ/mol; (b) phenol, $\text{C}_6\text{H}_5\text{OH}(\text{s})$, used as a disinfectant and in the production of thermo-setting plastics: $\Delta H_{\text{combustion}}^0 = -3053$ kJ/mol.

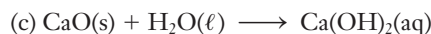
129. ▲ Standard entropy changes cannot be measured directly in the laboratory. They are calculated from experimentally obtained values of ΔG^0 and ΔH^0 . From the data given here, calculate ΔS^0 at 298 K for each of the following reactions.



$$\Delta H^0 = -323.2 \text{ kJ/mol} \quad \Delta G^0 = -358.4 \text{ kJ/mol}$$



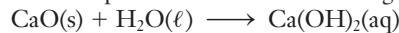
$$\Delta H^0 = -125.4 \text{ kJ/mol} \quad \Delta G^0 = -145.4 \text{ kJ/mol}$$



$$\Delta H^0 = 81.5 \text{ kJ/mol} \quad \Delta G^0 = -26.20 \text{ kJ/mol}$$

130. ▲ Calculate q , w , and ΔE for the vaporization of 12.5 g of liquid ethanol ($\text{C}_2\text{H}_5\text{OH}$) at 1.00 atm at 78.0°C, to form gaseous ethanol at 1.00 atm at 78.0°C. Make the following simplifying assumptions: (a) the density of liquid ethanol at 78.0°C is 0.789 g/mL, and (b) gaseous ethanol is adequately described by the ideal gas equation. The heat of vaporization of ethanol is 855 J/g.

131. We add 0.100 g of $\text{CaO}(\text{s})$ to 125 g H_2O at 23.6°C in a coffee-cup calorimeter. The following reaction occurs.



$$\Delta H^0 = 81.5 \text{ kJ/mol rxn}$$

What will be the final temperature of the solution?

132. (a) The accurately known molar heat of combustion of naphthalene, $\text{C}_{10}\text{H}_8(\text{s})$, $\Delta H = -5156.8$ kJ/mol C_{10}H_8 , is used to calibrate calorimeters. The complete combustion of 0.01520 g of C_{10}H_8 at constant pressure raises the temperature of a calorimeter by 0.212°C. Find the heat capacity of the calorimeter. (b) The initial temperature of the calorimeter (part a) is 22.102°C; 0.1040 g of $\text{C}_8\text{H}_{18}(\ell)$, octane (molar heat of combustion $\Delta H = -5451.4$ kJ/mol C_8H_{18}), is completely burned in the calorimeter. Find the final temperature of the calorimeter.

Conceptual Exercises

133. When a gas expands suddenly, it may not have time to absorb a significant amount of heat: $q = 0$. Assume that 1.00 mol N_2 expands suddenly, doing 3000. J of work. (a) What is ΔE for the process? (b) The heat capacity of N_2 is 20.9 J/mol °C. How much does its temperature fall during this expansion? (This is the principle of most snow-making machines, which use compressed air mixed with water vapor.)



134. As a rubber band is stretched, it gets warmer; when released, it gets cooler. To obtain the more nearly linear arrangement of the rubber band's polymeric material from the more random relaxed rubber band requires that there be rotation about carbon-carbon single bonds. Based on these data, give the sign of ΔG , ΔH , and ΔS for the stretching of a rubber band and for the relaxing of a stretched rubber band. What drives the spontaneous process?
135. (a) The decomposition of mercury(II) oxide has been used as a method for producing oxygen, but this is not a recommended method. Why? (b) Write the balanced equation for the decomposition of mercury(II) oxide. (c) Calculate the ΔH° , ΔS° , and ΔG° for the reaction. (d) Is the reaction spontaneous at room temperature?
136. (a) A student heated a sample of a metal weighing 32.6 g to 99.83°C and put it into 100.0 g of water at 23.62°C in a calorimeter. The final temperature was 24.41°C. The student calculated the specific heat of the metal, but neglected to use the heat capacity of the calorimeter. The specific heat of water is 4.184 J/g · °C. What was his answer? The metal was known to be chromium, molybdenum, or tungsten. By comparing the value of the specific heat to those of the metals (Cr, 0.460; Mo, 0.250; W, 0.135 J/g · °C), the student identified the metal. What was the metal? (b) A student at the next laboratory bench did the same experiment, obtained the same data, and used the heat capacity of the calorimeter in his calculations. The heat capacity of the calorimeter was 410. J/°C. Was his identification of the metal different?
137. According to the Second Law of Thermodynamics what would be the ultimate state or condition of the universe?
138. For each of the following changes, estimate the signs (positive, negative, or 0) of ΔS and ΔG .
 (a) The growth of a crystal from a supersaturated solution
 (b) Sugar cube + cup of hot tea $\longrightarrow$ cup of hot, sweetened tea
 (c) $\text{H}_2\text{O(s)} \longrightarrow \text{H}_2\text{O(l)}$
139. Estimate the boiling point of tin(IV) chloride, SnCl_4 , at one atmosphere pressure:



$$\text{SnCl}_4(\text{l}): \Delta H^\circ_{\text{f}} = -511.3 \text{ kJ/mol}, S^\circ = 258.6 \text{ J/mol} \cdot \text{K}$$

$$\text{SnCl}_4(\text{g}): \Delta H^\circ_{\text{f}} = -471.5 \text{ kJ/mol}, S^\circ = 366 \text{ J/mol} \cdot \text{K}$$

Building Your Knowledge

140. Energy to power muscular work is produced from stored carbohydrates (glycogen) or fat (triglycerides). Metabolic consumption and production of energy are described with the nutritional "Calorie," which is equal to 1 kilocalorie. Average energy output per minute for various activities follows: sitting, 1.7 kcal; walking, level, 3.5 mph, 5.5 kcal; cycling, level, 13 mph, 10. kcal; swimming, 8.4 kcal; running, 10. mph, 19 kcal. Approximate energy values of some common foods are also given: large apple, 100. kcal;

8-oz cola drink, 105 kcal; malted milkshake, 500. kcal; $\frac{3}{4}$ cup pasta with tomato sauce and cheese, 195 kcal; hamburger on bun with sauce, 350. kcal; 10.-oz sirloin steak, including fat, 1000. kcal. To maintain body weight, fuel intake should balance energy output. Prepare a table showing (a) each given food, (b) its fuel value, and (c) the minutes of each activity that would balance the kcal of each food.

141. From its heat of fusion, calculate the entropy change associated with the melting of one mole of ice at its melting point. From its heat of vaporization, calculate the entropy change associated with the boiling of one mole of water at its boiling point. Are your calculated values consistent with the simple model that we use to describe order in solids, liquids, and gases?
142. The energy content of dietary fat is 39 kJ/g, and for protein and carbohydrates it is 17 and 16 kJ/g, respectively. A 70.0-kg (155-lb) person utilizes 335 kJ/h while resting and 1250. kJ/h while walking 6 km/h. How many hours would the person need to walk per day instead of resting if he or she consumed 100. g (about $\frac{1}{4}$ lb) of fat instead of 100. g of protein in order to not gain weight?
143. The enthalpy change for melting one mole of water at 273 K is $\Delta H^\circ_{273} = 6010. \text{ J/mol}$, whereas that for vaporizing a mole of water at 373 K is $\Delta H^\circ_{273} = 40,660 \text{ J/mol}$. Why is the second value so much larger?
144. A 43.6-g chunk of lead was removed from a beaker of boiling water, quickly dried, and dropped into a polystyrene cup containing 50.0 g of water at 25.0°C. As the system reached equilibrium, the water temperature rose to 26.8°C. The heat capacity of the polystyrene cup had previously been determined to be 18.6 J/°C. Calculate the molar heat capacity and the specific heat of lead.
145. Methane, $\text{CH}_4(\text{g})$, is the main constituent of natural gas. In excess oxygen, methane burns to form $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$, whereas in limited oxygen, the products are $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{l})$. Which would result in a higher temperature: a gas-air flame or a gas-oxygen flame? How can you tell?



A methane flame

146. A 0.483-g sample of butter was burned in a bomb calorimeter whose heat capacity was 4572 J/°C, and the temperature was observed to rise from 24.76 to 27.93°C. Calculate the fuel value of butter in (a) kJ/g; (b) nutritional Calories/g (one nutritional Calorie is equal to one kilocalorie); (c) nutritional Calories/5-gram pat.

Beyond the Textbook

NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included, as an essential part of the answer.*

Go to a suitable site and find the answers to the next two questions about Germain Henri Hess.

147. Hess's Law is also known as the Law of _____.
148. Before he became a professor of chemistry at 28 years of age, what career did Germain Hess pursue?
149. Go to a website that describes the events in the life of Josiah Willard Gibbs.
(a) In what way was the doctorate degree granted to Gibbs, from whom Gibbs free energy gets its name, a first? (b) At what university did he spend nearly all his academic career?
150. Use the *Handbook of Chemistry and Physics* or another suitable reference to find the heats of formation of the following hydrocarbons: methane, ethane, propane, and *n*-butane. (a) What are the units of the values you have found? (b) Is there a trend when you compare the formula weight of each hydrocarbon with its heat of formation?
151. Why does $\text{Al}_2\text{O}_3(\text{s})$ have a lower entropy than $\text{Fe}_2\text{O}_3(\text{s})$? There are two primary qualitative reasons for this. You may have to use the chemistry library or some other source to get more information on the properties of these two common compounds to answer the question.
152. Steel is made by the high-temperature reaction of iron oxide (Fe_2O_3) with coke (a form of carbon) to produce metallic iron and CO_2 . This same reaction can NOT be done with alumina (Al_2O_3) and carbon to make metallic Al and CO_2 . Why not? Explain fully and give thermodynamic reasons for your answer. You may need to obtain further information from outside sources on the properties of the substances involved.



Chemical Kinetics

16



A burning building is an example of a rapid, highly exothermic reaction. Firefighters use basic principles of chemical kinetics to battle the fire. When water is sprayed onto a fire, its evaporation absorbs a large amount of energy; this lowers the temperature and slows the reaction. Other common methods for extinguishing fires include covering them with CO_2 (used in some fire extinguishers), which decreases the supply of oxygen, and backburning (for grass and forest fires), which removes combustible material. In both cases, the removal of a reactant slows (or stops) the reaction.

Lincoln Potter/Tony Stone Images

OUTLINE

16-1 The Rate of a Reaction

Factors That Affect Reaction Rates

16-2 Nature of the Reactants

16-3 Concentrations of Reactants: The Rate-Law Expression

16-4 Concentration Versus Time: The Integrated Rate Equation

16-5 Collision Theory of Reaction Rates

16-6 Transition State Theory

16-7 Reaction Mechanisms and the Rate-Law Expression

16-8 Temperature: The Arrhenius Equation

16-9 Catalysts

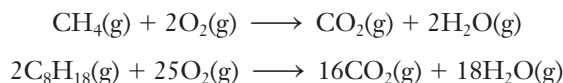
OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Express the rate of a chemical reaction in terms of changes in concentrations of reactants and products with time
- ▶ Describe the experimental factors that affect the rates of chemical reactions
- ▶ Use the rate-law expression for a reaction—the relationship between concentration and rate
- ▶ Use the concept of order of a reaction
- ▶ Apply the method of initial rates to find the rate-law expression for a reaction
- ▶ Use the integrated rate-law expression for a reaction—the relationship between concentration and time
- ▶ Analyze concentration-versus-time data to determine the order of a reaction
- ▶ Describe the collision theory of reaction rates
- ▶ Describe the main aspects of transition state theory and the role of activation energy in determining the rate of a reaction
- ▶ Explain how the mechanism of a reaction is related to its rate-law expression
- ▶ Predict the rate-law expression that would result from a proposed reaction mechanism
- ▶ Identify reactants, products, intermediates, and catalysts in a multistep reaction mechanism
- ▶ Explain how temperature affects rates of reactions
- ▶ Use the Arrhenius equation to relate the activation energy for a reaction to changes in its rate constant with changing temperature
- ▶ Explain how a catalyst changes the rate of a reaction
- ▶ Describe homogeneous catalysis and heterogeneous catalysis

We are all familiar with processes in which some quantity changes with time—a car travels at 40 miles/hour, a faucet delivers water at 3 gallons/minute, or a factory produces 32,000 tires/day. Each of these ratios is called a rate. The **rate of a reaction** describes how fast reactants are used up and products are formed. **Chemical kinetics** is the study of rates of chemical reactions, the factors that affect reaction rates, and the mechanisms (the series of steps) by which reactions occur.

Our experience tells us that different chemical reactions occur at very different rates. For instance, combustion reactions—such as the burning of methane, CH_4 , in natural gas and the combustion of isooctane, C_8H_{18} , in gasoline—proceed very rapidly, sometimes even explosively.

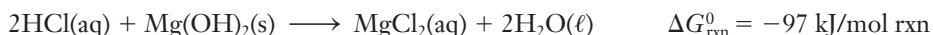


On the other hand, the rusting of iron occurs only very slowly.

Understanding and controlling the rates of reactions is critically important in nearly all areas. In any living system, a huge number of reactions must all interconnect smoothly. Plants and animals use many different ways, all based on the ideas of this chapter, to provide materials from one reaction at rates and in amounts needed for subsequent reactions. Illnesses often disrupt the normal control of reaction rates. The preservation of food by refrigeration uses lowered temperatures to slow the rate of unwanted spoilage reactions. Similarly, chemical engineers use the concepts of chemical kinetics to develop conditions to produce desired materials at a useful and economic rate, while slowing unwanted side reactions and avoiding dangerously high reaction rates that might lead to explosions.

In our study of thermodynamics, we learned to assess whether a particular reaction was spontaneous or not and how much energy was released or absorbed. The question of how rapidly a reaction proceeds is addressed by kinetics. Even though a reaction is thermodynamically spontaneous, it might not occur at a measurable rate.

The reactions of strong acids with strong bases are thermodynamically favored and occur at very rapid rates. Consider, for example, the reaction of hydrochloric acid solution with solid magnesium hydroxide. It is thermodynamically spontaneous at standard state conditions, as indicated by the negative ΔG_{rxn}^0 value. It also occurs rapidly.



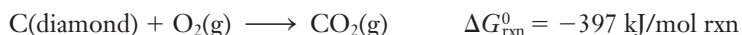
STOP & THINK

Remember that *spontaneous* is a thermodynamic term for a reaction that releases free energy, which could potentially be used to do work. It does not mean that a reaction is *instantaneous* (extremely fast). Only by studying the kinetics of a spontaneous reaction can we determine how rapidly it will proceed.

- ▶ This is one of the reactions that occurs in a human digestive system when an antacid containing relatively insoluble magnesium hydroxide neutralizes excess stomach acid.

Unless otherwise noted, all content on this page is © Cengage Learning.

The reaction of diamond with oxygen is also thermodynamically spontaneous.



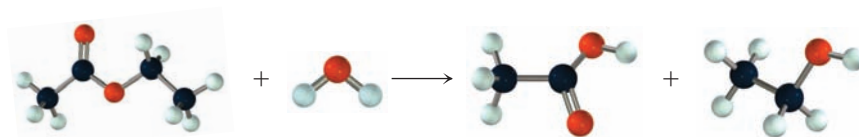
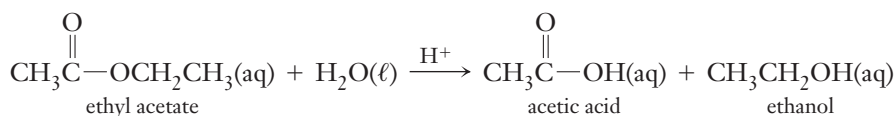
However, we know from experience that diamonds exposed to the oxygen in air, even over long periods, do not react to form carbon dioxide. The reaction does not occur at an observable rate near room temperature, but diamonds will burn when heated to a high enough temperature in the presence of oxygen.

The reaction of graphite with oxygen is also spontaneous, with a similar value of $\Delta G_{\text{rxn}}^0 = -394 \text{ kJ/mol rxn}$. Once it is started, this reaction occurs rapidly. These observations of reaction speeds are explained by kinetics, not thermodynamics.

16-1 The Rate of a Reaction

Rates of reactions are usually expressed in units of moles per liter per unit time. If we know the chemical equation for a reaction, its rate can be determined by following the change in concentration of any product or reactant that can be detected quantitatively.

To describe the rate of a reaction, we must determine the concentration of a reactant or product at various times as the reaction proceeds. Devising effective methods for measuring these concentrations is a continuing challenge for chemists who study chemical kinetics. If a reaction is slow enough, we can take samples from the reaction mixture after successive time intervals and then analyze them. For instance, if one reaction product is an acid, its concentration can be determined by titration (see Section 11-2) after each time interval. The reaction of ethyl acetate with water in the presence of a small amount of strong acid produces acetic acid. The extent of the reaction at any time can be determined by titration of the acetic acid.



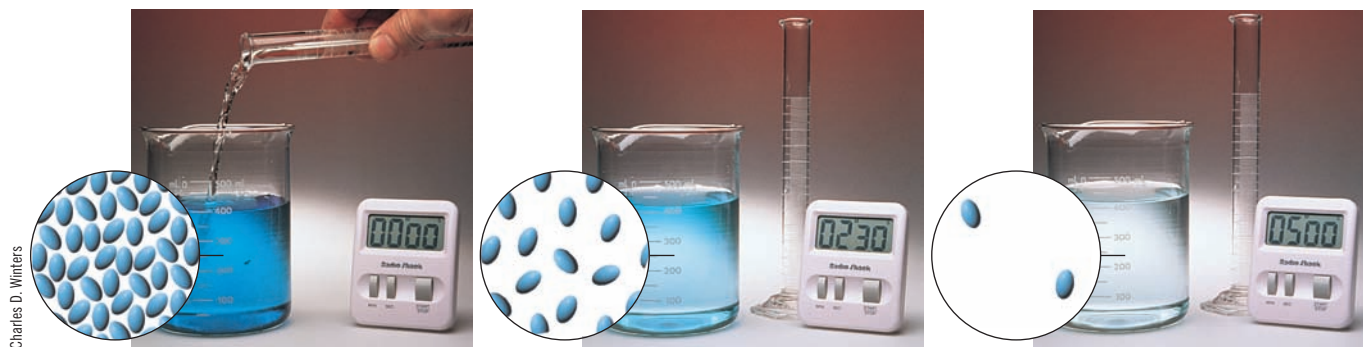
This approach is suitable only if the reaction is sufficiently slow that the time elapsed during withdrawal and analysis of the sample is negligible. Sometimes the sample is withdrawn and then quickly cooled (“quenched”). This slows the reaction (see Section 16-8) so much that the desired concentration does not change significantly while the analysis is performed.

It is more convenient, especially when a reaction is rapid, to use a technique that continually monitors the change in some physical property of the system. If one of the reactants or products is colored, the increase (or decrease) in intensity of its color might be used to measure a decrease or increase in its concentration. Such an experiment is a special case of *spectroscopic* methods. These methods involve passing light (visible, infrared, or ultraviolet) through the sample. The light should have a wavelength that is absorbed by some substance whose concentration is changing (Figure 16-1). An appropriate light-sensing apparatus provides a signal that depends on the concentration of the absorbing substance. Modern techniques that use computer-controlled pulsing and sensing of lasers have enabled scientists to sample concentrations at very frequent intervals on the order of picoseconds (1 picosecond = 10^{-12} second) or even femtoseconds (1 femtosecond = 10^{-15} second). Such studies have yielded information about very fast reactions, such as energy transfer resulting from absorption of light in photosynthesis.

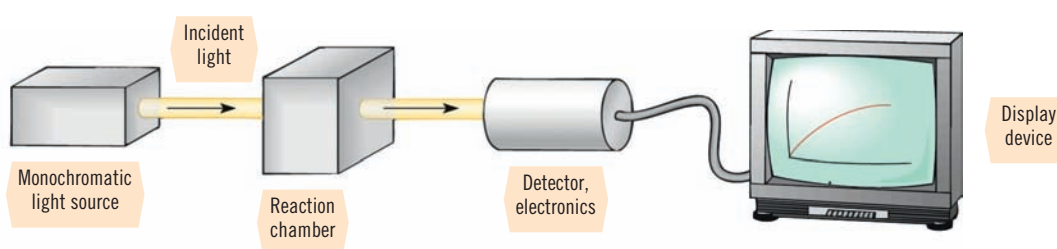
► Recall that the units kJ/mol rxn refer to the numbers of moles of reactants and products in the balanced equation. The units kJ/mol rxn are often shortened to kJ/mol.



Propane burning is a very rapid reaction.



A Blue dye is reacting with bleach, which converts it into a colorless product. The color decreases and eventually disappears. The rate of the reaction could be determined by repeatedly measuring both the color intensity and the elapsed time. The concentration of dye could be calculated from the intensity of the blue color. (Only unreacted dye molecules are shown for clarity.)



B A schematic of a method for determining reaction rates is shown. Light of a wavelength that is absorbed by some substance whose concentration is changing is passed through a reaction chamber. Recording the change in light intensity gives a measure of the changing concentration of a reactant or product as the reaction progresses.

Figure 16-1 Monitoring a reaction via a change in color intensity.

► In reactions involving gases, rates of reactions may be related to rates of change of partial pressures. Pressures of gases and concentrations of gases are directly proportional.

$$PV = nRT \quad \text{or} \quad P = \frac{n}{V} RT = MRT$$

where M is molarity.

If the progress of a reaction causes a change in the total number of moles of gas present, the change in pressure of the reaction mixture (held at constant temperature and constant volume) lets us measure how far the reaction has gone. For instance, the decomposition of dinitrogen pentoxide, $\text{N}_2\text{O}_5(\text{g})$, has been studied by this method.



For every two moles of N_2O_5 gas that react, a total of five moles of gas is formed (four moles of NO_2 and one mole of O_2). The resulting increase in pressure can be related by the ideal gas equation to the total number of moles of gas present. This indicates the extent to which the reaction has occurred.

Once we have measured the changes in concentrations of reactants or products with time, how do we describe the rate of a reaction? Consider a hypothetical reaction.

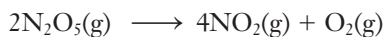


In this generalized representation, a represents the coefficient of substance A in the balanced chemical equation, b is the coefficient of substance B, and so on. For example, in the equation for the decomposition of N_2O_5 , A would represent the reactant N_2O_5 , with $a = 2$; C would be the first product NO_2 , with $c = 4$; and D the remaining product O_2 , with $d = 1$.

The amount of each substance present can be given by its concentration, usually expressed as molarity (mol/L) and designated by brackets. The rate at which the reaction proceeds can be described in terms of the rate at which one of the reactants disappears, $-\Delta[\text{A}]/\Delta t$ or $-\Delta[\text{B}]/\Delta t$, or the rate at which one of the products appears, $\Delta[\text{C}]/\Delta t$ or $\Delta[\text{D}]/\Delta t$. The reaction rate must be positive because it describes the forward (left-to-right) reaction, which consumes A and B. The concentrations of reactants A and B decrease in the time interval Δt . Thus, $\Delta[\text{A}]/\Delta t$ and $\Delta[\text{B}]/\Delta t$ would be *negative* quantities. The purpose of the negative sign in the definition when using a reactant is to make the *reaction rate* positive.

► The Greek “delta,” Δ , stands for “change in,” just as it did in Chapter 15.

Changes in concentration are related to one another by the stoichiometry of the balanced equation. For every a mol/L that $[A]$ decreases, $[B]$ must decrease by b mol/L, $[C]$ must increase by c mol/L, and so on. In the case of the N_2O_5 reaction:



NO_2 is produced at a rate $\frac{4}{2}$ or twice as fast as N_2O_5 disappears. O_2 , on the other hand, is produced $\frac{1}{2}$ or half as fast as N_2O_5 is consumed.

We wish to describe the rate of reaction on a basis that is the same regardless of which reactant or product we choose to measure. To do this, we can describe the number of *moles of reaction* that occur per liter in a given time. For instance, this is accomplished for reactant A as

$$\left(\frac{1 \text{ mol rxn}}{a \text{ mol A}}\right) \left(\frac{\text{rate of decrease}}{\text{in } [A]}\right) = -\left(\frac{1 \text{ mol rxn}}{a \text{ mol A}}\right) \left(\frac{\Delta[A]}{\Delta t}\right)$$

The units for rate of reaction are $\frac{\text{mol rxn}}{\text{L} \cdot \text{time}}$, which we usually shorten to $\frac{\text{mol}}{\text{L} \cdot \text{time}}$ or $\text{mol} \cdot \text{L}^{-1} \cdot \text{time}^{-1}$. The units $\frac{\text{mol}}{\text{L}}$ represent molarity, M , so the units for rate of reaction can also be written as $\frac{M}{\text{time}}$ or $M \cdot \text{time}^{-1}$. Similarly, we can divide each concentration change by its coefficient in the balanced equation. Bringing signs to the beginning of each term, we write the rate of reaction based on the rate of change of concentration of each species.

$$\begin{aligned} \text{rate of reaction} &= \overbrace{\frac{1}{a} \left(\frac{\text{rate of decrease}}{\text{in } [A]} \right)}^{\text{in terms of reactants}} = \overbrace{\frac{1}{b} \left(\frac{\text{rate of decrease}}{\text{in } [B]} \right)}^{\text{in terms of reactants}} = \overbrace{\frac{1}{c} \left(\frac{\text{rate of increase}}{\text{in } [C]} \right)}^{\text{in terms of products}} = \overbrace{\frac{1}{d} \left(\frac{\text{rate of increase}}{\text{in } [D]} \right)}^{\text{in terms of products}} \\ \text{rate of reaction} &= -\frac{1}{a} \left(\frac{\Delta[A]}{\Delta t} \right) = -\frac{1}{b} \left(\frac{\Delta[B]}{\Delta t} \right) = \frac{1}{c} \left(\frac{\Delta[C]}{\Delta t} \right) = \frac{1}{d} \left(\frac{\Delta[D]}{\Delta t} \right) \end{aligned}$$

This representation gives several equalities, any one of which can be used to relate changes in observed concentrations to the rate of reaction.

The expressions just given describe the *average* rate over some finite time period Δt . The rigorous expressions for the rate at any instant involve the derivatives of concentrations with respect to time.

$$-\frac{1}{a} \left(\frac{d[A]}{dt} \right), \frac{1}{c} \left(\frac{d[C]}{dt} \right), \text{ and so on.}$$

The shorter the time period, the closer $\frac{\Delta(\text{concentration})}{\Delta t}$ is to the corresponding derivative.

STOP & THINK

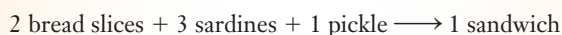
The *relative* reaction rates for the disappearance of reactants and formation of products are based on the reaction stoichiometries.

► Time units are usually expressed in seconds and abbreviated as s. Occasionally, minutes (min), hours (h), or years (y) are used for slower reactions.



Problem-Solving Tip Signs and Divisors in Expressions for Rate

As an analogy to these chemical reaction rate expressions, suppose we make sardine sandwiches by the following procedure:



As time goes by, the number of sandwiches increases, so $\Delta(\text{sandwiches})$ is positive; the rate of the process is given by $\Delta(\text{sandwiches})/\Delta(\text{time})$. Alternatively, we would count the decreasing number of pickles at various times. Because $\Delta(\text{pickles})$ is

negative, we must multiply by (-1) to make the rate positive; rate = $-\Delta(\text{pickles})/\Delta(\text{time})$. If we measure the rate by counting slices of bread, we must also take into account that bread slices are consumed *twice as fast* as sandwiches are produced, so rate = $-\frac{1}{2}(\Delta(\text{bread})/\Delta(\text{time}))$. Four different ways of describing the rate all have the same numerical value.

$$\text{rate} = \left(\frac{\Delta(\text{sandwiches})}{\Delta t} \right) = -\frac{1}{2} \left(\frac{\Delta(\text{bread})}{\Delta t} \right) = -\frac{1}{3} \left(\frac{\Delta(\text{sardines})}{\Delta t} \right) = - \left(\frac{\Delta(\text{pickles})}{\Delta t} \right)$$

Consider as a specific chemical example the gas-phase reaction that occurs when we mix 1.000 mole of hydrogen and 2.000 moles of iodine chloride at 230°C in a closed 1.000-liter container.



The coefficients tell us that one mole of H_2 disappears for every two moles of ICl that disappear and for every one mole of I_2 and two moles of HCl that are formed. In other terms, the rate of disappearance of moles of H_2 is one-half the rate of disappearance of moles of ICl , and so on. So we write the rate of reaction as

$$\begin{aligned} \text{rate of reaction} &= \overbrace{\left(\frac{\text{rate of decrease in } [\text{H}_2]}{\text{in } [\text{H}_2]} \right)}^{\text{in terms of reactants}} = \frac{1}{2} \overbrace{\left(\frac{\text{rate of decrease in } [\text{ICl}]}{\text{in } [\text{ICl}]} \right)}^{\text{in terms of reactants}} = \overbrace{\left(\frac{\text{rate of increase in } [\text{I}_2]}{\text{in } [\text{I}_2]} \right)}^{\text{in terms of products}} = \frac{1}{2} \overbrace{\left(\frac{\text{rate of increase in } [\text{HCl}]}{\text{in } [\text{HCl}]} \right)}^{\text{in terms of products}} \\ \text{rate of reaction} &= - \left(\frac{\Delta[\text{H}_2]}{\Delta t} \right) = -\frac{1}{2} \left(\frac{\Delta[\text{ICl}]}{\Delta t} \right) = \left(\frac{\Delta[\text{I}_2]}{\Delta t} \right) = \frac{1}{2} \left(\frac{\Delta[\text{HCl}]}{\Delta t} \right) \end{aligned}$$

STOP & THINK

Suppose a driver travels 40 miles in an hour; we describe his average speed (rate) as 40 mi/h. This does not necessarily mean that he drove at a steady speed. He might have stopped at a few traffic signals, made a fuel stop, driven sometimes faster, sometimes slower—his *instantaneous rate* (the rate at which he was traveling at any instant) was quite changeable.

Table 16-1 lists the concentrations of reactants remaining at 1-second intervals, beginning with the time of mixing ($t = 0$ seconds). The *average* rate of reaction over each 1-second interval is indicated in terms of the rate of decrease in concentration of hydrogen. Verify for yourself that the rate of loss of ICl is twice that of H_2 . Therefore, the rate of reaction could also be expressed as rate = $-\frac{1}{2}(\Delta[\text{ICl}]/\Delta t)$. Increases in concentration of products could be used instead. Figure 16-2 shows graphically the rates of change of concentrations of all reactants and products.

Table 16-1 Concentration and Rate Data for Reaction of 2.000 M ICl and 1.000 M H_2 at 230°C

$\text{H}_2(\text{g}) + 2\text{ICl}(\text{g}) \longrightarrow \text{I}_2(\text{g}) + 2\text{HCl}(\text{g})$		Average Rate During Time Interval = $-\frac{\Delta[\text{H}_2]}{\Delta t}$		Time (t) (seconds)
$[\text{ICl}]$ (mol/L)	$[\text{H}_2]$ (mol/L)	$(M \cdot s^{-1})$		
2.000	1.000			0
1.348	0.674	0.326		1
1.052	0.526	0.148		2
0.872	0.436	0.090		3
0.748	0.374	0.062		4
0.656	0.328	0.046		5
0.586	0.293	0.035		6
0.530	0.265	0.028		7
0.484	0.242	0.023		8

► For example, the *average* rate over the interval from 1 to 2 seconds can be calculated as

$$\begin{aligned} -\frac{\Delta[\text{H}_2]}{\Delta t} &= \\ &= \frac{(0.526 - 0.674) \text{ mol} \cdot \text{L}^{-1}}{(2 - 1) \text{ s}} \\ &= 0.148 \text{ mol} \cdot \text{L}^{-1} \text{ s}^{-1} \\ &= 0.148 \text{ M} \cdot \text{s}^{-1} \end{aligned}$$

This does *not* mean that the reaction proceeds at this rate during the entire interval.

Unless otherwise noted, all content on this page is © Cengage Learning.

Figure 16-3 is a plot of the hydrogen concentration versus time, using data from Table 16-1. The initial rate, or the rate at the instant of mixing the reactants, is the negative of the slope at $t = 0$. The *instantaneous* rate of reaction at time t (2.0 seconds, for example) is the negative of the slope of the tangent to the curve at time t . We see that the rate decreases with time; lower concentrations of H_2 and ICl result in slower reaction. Had we plotted concentration of a product versus time, the rate would have been related to the *positive* slope of the tangent at time t .

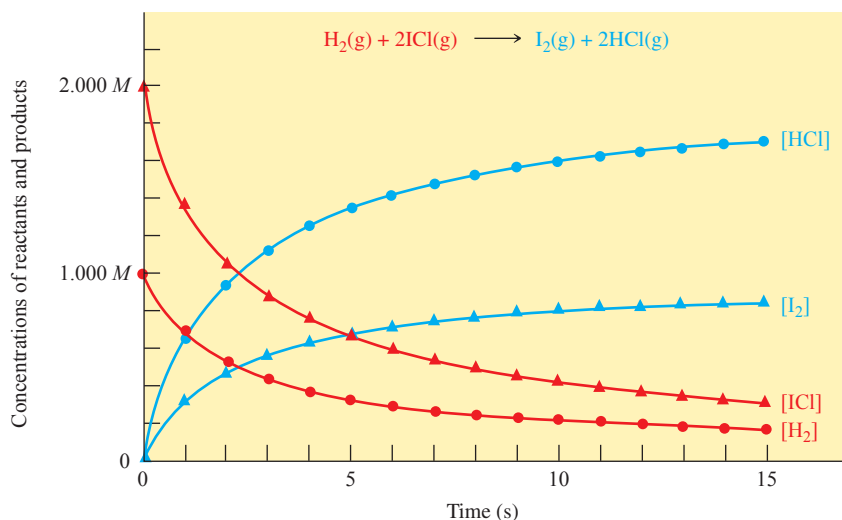


Figure 16-2 Plot of concentrations of all reactants and products versus time in the reaction of 1.000 M H_2 with 2.000 M ICl at 230°C, from data in Table 16-1 (and a few more points).

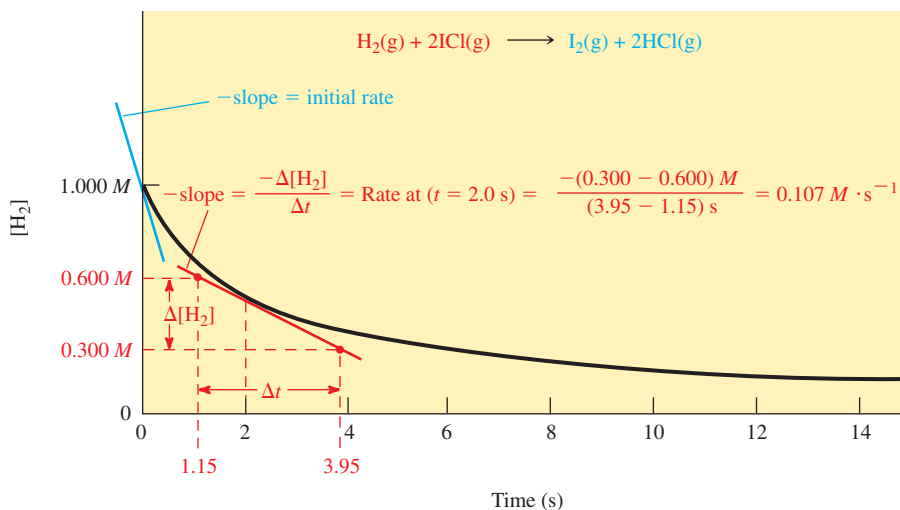


Figure 16-3 Plot of H_2 concentration versus time for the reaction of 1.000 M H_2 with 2.000 M ICl . The instantaneous rate of reaction at any time, t , equals the negative of the slope of the tangent to this curve at time t . The initial rate of the reaction is equal to the negative of the initial slope ($t = 0$). The determination of the instantaneous rate at $t = 2$ seconds is illustrated. (If you do not recall how to find the slope of a straight line, refer to Figure 16-5.)

EXAMPLE 16-1 Rate of Reaction

At some time, we observe that the reaction $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ is forming NO_2 at the rate of $0.0072 \frac{\text{mol}}{\text{L} \cdot \text{s}}$.

- What is the rate of change of $[\text{O}_2]$, $\frac{\Delta[\text{O}_2]}{\Delta t}$, in $\frac{\text{mol}}{\text{L} \cdot \text{s}}$, at this time?
- What is the rate of change of $[\text{N}_2\text{O}_5]$, $\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$, in $\frac{\text{mol}}{\text{L} \cdot \text{s}}$, at this time?
- What is the rate of reaction at this time?

Plan

We can use the mole ratios (stoichiometry) from the balanced equation to determine the rates of change of other products and reactants. The rate of reaction can then be derived from any one of these individual rates.

Solution

- (a) The balanced equation gives the reaction ratio $\frac{1 \text{ mol O}_2}{4 \text{ mol NO}_2}$.

$$\text{rate of change of } [\text{O}_2] = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{0.0072 \text{ mol NO}_2}{\text{L} \cdot \text{s}} \times \frac{1 \text{ mol O}_2}{4 \text{ mol NO}_2} = 0.0018 \frac{\text{mol O}_2}{\text{L} \cdot \text{s}}$$

- (b) The balanced equation shows that 2 mol N_2O_5 is *consumed* for every 4 mol NO_2 that is *formed*. Because $[\text{N}_2\text{O}_5]$ is decreasing as $[\text{NO}_2]$ increases, we should write the reaction

$$\text{ratio as } \frac{-2 \text{ mol N}_2\text{O}_5}{4 \text{ mol NO}_2}.$$

$$\begin{aligned} \text{rate of change of } [\text{N}_2\text{O}_5] &= \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{0.0072 \text{ mol NO}_2}{\text{L} \cdot \text{s}} \times \frac{-2 \text{ mol N}_2\text{O}_5}{4 \text{ mol NO}_2} \\ &= -0.0036 \frac{\text{mol N}_2\text{O}_5}{\text{L} \cdot \text{s}} \end{aligned}$$

► The concentration of N_2O_5 is decreasing, so its rate of change is negative.

The rate of *change* of $[\text{N}_2\text{O}_5]$ with time, $\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$, is $-0.0036 \frac{\text{mol N}_2\text{O}_5}{\text{L} \cdot \text{s}}$, a *negative* number, because N_2O_5 , a reactant, is being used up.

- (c) The rate of reaction can be calculated from the rate of decrease of any reactant concentration or the rate of increase of any product concentration.

$$\text{rate of reaction} = -\frac{1}{2} \left(\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} \right) = -\frac{1}{2} \left(-0.0036 \frac{\text{mol}}{\text{L} \cdot \text{s}} \right) = 0.0018 \frac{\text{mol}}{\text{L} \cdot \text{s}}$$

$$\text{rate of reaction} = \frac{1}{4} \left(\frac{\Delta[\text{NO}_2]}{\Delta t} \right) = \frac{1}{4} \left(0.0072 \frac{\text{mol}}{\text{L} \cdot \text{s}} \right) = 0.0018 \frac{\text{mol}}{\text{L} \cdot \text{s}}$$

$$\text{rate of reaction} = \frac{1}{1} \left(\frac{\Delta[\text{O}_2]}{\Delta t} \right) = 0.0018 \frac{\text{mol}}{\text{L} \cdot \text{s}}$$

We see that the rate of reaction is the same, no matter which reactant or product we use to determine it. Remember that the mol in these units is interpreted as “moles of reaction.”

You should now work Exercise 10.

STOP & THINK

Always remember to divide by the balanced reactant or product coefficients in order to convert the individual reactant and product rates into an overall reaction rate. The overall reaction rate is always positive and expressed on a per mole basis.

Factors That Affect Reaction Rates

Often we want a reaction to take place rapidly enough to be practical but not so rapidly as to be dangerous. The controlled burning of fuel in an internal combustion engine is an example of such a process. On the other hand, we want some undesirable reactions, such as the spoiling of food, to take place more slowly.

Four factors have marked effects on the rates of chemical reactions.

1. Nature of the reactants
2. Concentrations of the reactants
3. Temperature
4. The presence of a catalyst

Understanding the effects of these factors can help us control the rates of reactions in desirable ways. The study of these factors gives important insight into the details of the pro-

cesses by which a reaction occurs. This kind of study is the basis for developing theories of chemical kinetics. We will now study these factors and the related theories—collision theory and transition state theory.

16-2 Nature of the Reactants

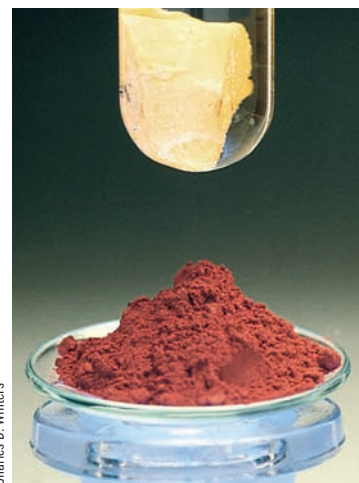
The physical states of reacting substances are important in determining their reactivities. A puddle of liquid gasoline can burn smoothly, but gasoline vapors can burn explosively. Two immiscible liquids may react slowly at their interface, but if they are mixed to provide better contact, the reaction speeds up. White phosphorus and red phosphorus are different solid forms (allotropes) of elemental phosphorus. White phosphorus ignites when exposed to oxygen in the air. By contrast, red phosphorus can be kept in open containers for long periods of time without noticeable reaction.

Samples of dry solid potassium sulfate, K_2SO_4 , and dry solid barium nitrate, $\text{Ba}(\text{NO}_3)_2$, can be mixed with no appreciable reaction occurring for several years. But if aqueous solutions of the two are mixed, a reaction occurs rapidly, forming a white precipitate of barium sulfate.



Chemical identities of elements and compounds affect reaction rates. Metallic sodium, with its low ionization energy and strong reducing capability, reacts rapidly with water at room temperature; metallic calcium has a higher ionization energy and reacts only slowly with water at room temperature. Solutions of a strong acid and a strong base react rapidly when they are mixed because the interactions involve mainly electrostatic attractions between ions in solution. Reactions that involve the breaking of covalent bonds are usually slower.

The extent of subdivision of solids or liquids can be crucial in determining reaction rates. Large chunks of most metals do not burn. But many powdered metals, with larger surface areas and hence more atoms exposed to the oxygen of the air, burn easily. One pound of fine iron wire rusts much more rapidly than a solid one-pound chunk of iron. Violent explosions sometimes occur in grain elevators, coal mines, and chemical plants in which large amounts of powdered substances are produced. These explosions are examples of the effect of large surface areas on rates of reaction. The rate of reaction depends on the surface area or degree of subdivision. The ultimate degree of subdivision would make all reactant molecules (or ions or atoms) accessible to react at any given time. This situation can be achieved when the reactants are in the gaseous state or in solution.



Two allotropes of phosphorus. White phosphorus (*above*) ignites and burns rapidly when exposed to oxygen in the air, so it is stored under water. Red phosphorus (*below*) reacts with air much more slowly, so it can be stored in contact with air.



Powdered iron burns very rapidly when heated in a flame. Iron oxide is formed.



Powdered chalk (mostly calcium carbonate, CaCO_3) reacts rapidly with dilute hydrochloric acid because it has a large total surface area. A stick of chalk has a much smaller surface area, so it reacts much more slowly.

16-3 Concentrations of Reactants: The Rate-Law Expression

As the concentrations of reactants change at constant temperature, the rate of reaction changes. We write the **rate-law expression** (often called simply the **rate law**) for a reaction to describe how its rate depends on concentrations; this rate law is experimentally deduced for each reaction from a study of how its rate varies with concentration.

Unless otherwise noted, all content on this page is © Cengage Learning.

The rate-law expression for a reaction in which A, B, . . . are reactants has the general form

$$\text{rate} = k[A]^x[B]^y \dots$$

The constant k is called the **specific rate constant** (or just the **rate constant**) for the reaction at a particular temperature. The values of the exponents, x and y , and of the rate constant, k , bear no necessary relationship to the coefficients in the *balanced chemical equation* for the overall reaction and must be determined *experimentally*.

The powers to which the concentrations are raised, x and y , are usually small integers or zero but are occasionally fractional or even negative. A power of *one* means that the rate is directly proportional to the concentration of that reactant. A power of *two* means that the rate is directly proportional to the *square* of that concentration. A power of *zero* means that the rate does not depend on the concentration of that reactant, *so long as some of the reactant is present*. The value of x is said to be the order of the reaction with respect to A, and y is the order of the reaction with respect to B. The overall **order of the reaction** is the sum of the reactant orders, $x + y$. Examples of observed rate laws for some reactions follow.

► The order of the reaction with respect to a reactant is usually called simply the order of that reactant. The word *order* is used in kinetics in its mathematical meaning.



second order in NO; second order overall



first order in NO₂ and first order in F₂;
second order overall



second order in NO₂;
second order overall

► Any number raised to the zero power is one. Here $[\text{H}^+]^0 = 1$.



first order in H₂O₂ and first order in I[−];
zero order in H⁺; second order overall

We see that the orders (exponents) in the rate law expression *may* or *may not* match the coefficients in the balanced equation. There is *no* way to predict reaction orders from the balanced overall chemical equation. The orders must be determined experimentally.

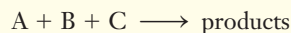
► More details about values and units of k will be discussed in later sections.

It is important to remember the following points about the specific rate constant, k .

1. Experimental data must first be used to determine the reaction orders and then the value of k for the reaction at appropriate conditions.
2. The value we determine is for a *specific reaction*, represented by a balanced equation.
3. The units of k depend on the *overall order* of the reaction.
4. The value we determine does not change with concentrations of either reactants or products.
5. The value we determine does not change with time (Section 16-4).
6. The value we determine refers to the reaction *at a particular temperature* and changes if we change the temperature (Section 16-8).
7. The value we determine depends on whether a *catalyst* is present and on the nature of the catalyst (Section 16-9).

EXAMPLE 16-2 Interpretation of the Rate Law

For a hypothetical reaction



the rate law is determined to be

$$\text{rate} = k[\text{A}][\text{B}]^2$$

What happens to the reaction rate when we make each of the following concentration changes?

(a) We triple the concentration of A without changing the concentration of B or C. (b) We triple the concentration of B without changing the concentration of A or C. (c) We triple the concentration of C without changing the concentration of A or B. (d) We triple all three concentrations simultaneously.

Plan

We interpret the rate law to predict the changes in reaction rate. We remember that changing concentrations of reactants does not change the value of k .

Solution

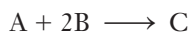
- (a) We see that rate is directly proportional to the *first power* of [A]. We do not change [B] or [C]. Tripling [A] (i.e., increasing [A] by a factor of 3) causes the reaction rate to increase by a factor of $3^1 = 3$ so the reaction rate triples.
- (b) We see that rate is directly proportional to the *second power* of [B], that is $[\text{B}]^2$. We do not change [A] or [C]. Tripling [B] (i.e., increasing [B] by a factor of 3) causes the reaction rate to increase by a factor of $3^2 = 9$.
- (c) The reaction rate is independent of [C] (zero order), so changing [C] causes no change in reaction rate ($3^0 = 1$).
- (d) Tripling all concentrations would cause the changes described in (a), (b), and (c) simultaneously. The rate would increase by a factor of 3 due to the change in [A], by a factor of 9 due to the change in [B], and be unaffected by the change in [C]. The result is that the reaction rate increases by a factor of $3^1 \times 3^2 = 3 \times 9 = 27$.

You should now work Exercises 14 and 15.

STOP & THINK

The concentration change is raised to the power represented by the order of that reactant. A common mistake is to multiply the concentration change by the order and not raise it to that power.

We can use the **method of initial rates** to deduce the rate law from experimentally measured rate data. Usually we know the concentrations of all reactants at the start of the reaction. We can then measure the initial rate of the reaction, corresponding to these initial concentrations. The following tabulated data refer to the hypothetical reaction



at a specific temperature. The brackets indicate the concentrations of the reacting species *at the beginning* of each experimental run listed in the first column—that is, the initial concentrations for each experiment.

► In such an experiment, we often keep some initial concentrations the same and vary others by simple factors, such as 2 or 3. This makes it easier to assess the effect of each change on the rate.

Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of C
1	$1.0 \times 10^{-2} \text{ M}$	$1.0 \times 10^{-2} \text{ M}$	$1.5 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$
2	$1.0 \times 10^{-2} \text{ M}$ — no change	$2.0 \times 10^{-2} \text{ M}$ — $\times 2$	$3.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}$ — $\times 2$
3	$2.0 \times 10^{-2} \text{ M}$ — $\times 2$	$2.0 \times 10^{-2} \text{ M}$ — no change	$1.2 \times 10^{-5} \text{ M} \cdot \text{s}^{-1}$ — $\times 4$

Unless otherwise noted, all content on this page is © Cengage Learning.

Because we are describing the same reaction in each experiment, each is governed by the same rate-law expression. This expression has the form

$$\text{rate} = k[A]^x[B]^y$$

Let's compare the initial rates of formation of product (reaction rates) for different experimental runs to see how changes in concentrations of reactants affect the rate of reaction. This lets us calculate the values of x and y , and then k .

We see that the initial concentration of A is the same in experiments 1 and 2; for these trials, any change in reaction rate would be due to different initial concentrations of B. Comparing these two experiments, we see that [B] has been changed by a factor of

$$\frac{2.0 \times 10^{-2}}{1.0 \times 10^{-2}} = 2.0 = [\text{B}] \text{ ratio}$$

The rate changes by a factor of

$$\frac{3.0 \times 10^{-6}}{1.5 \times 10^{-6}} = 2.0 = \text{rate ratio}$$

The exponent y can be deduced from

$$\begin{aligned} \text{rate ratio} &= ([\text{B}] \text{ ratio})^y \\ 2.0 &= (2.0)^y \quad \text{so} \quad y = 1 \end{aligned}$$

The reaction is first order in [B]. Thus far we know that the rate-law expression is

$$\text{rate} = k[A]^x[B]^1$$

To evaluate x , we observe that the concentrations of [A] are different in experiments 2 and 3. For these two trials, the initial concentration of B is the same, so any change in reaction rate could only be due to different initial concentrations of A. Comparing these two experiments, we see that [A] has been increased by a factor of

$$\frac{2.0 \times 10^{-2}}{1.0 \times 10^{-2}} = 2.0 = [\text{A}] \text{ ratio}$$

The rate increases by a factor of

$$\frac{1.2 \times 10^{-5}}{3.0 \times 10^{-6}} = 4.0 = \text{rate ratio}$$

The exponent x can be deduced from

$$\begin{aligned} \text{rate ratio} &= ([\text{A}] \text{ ratio})^x \\ 4.0 &= (2.0)^x \quad \text{so} \quad x = 2 \end{aligned}$$

The reaction is second order in [A]. We can now write its rate-law expression as

$$\text{rate} = k[A]^2[B]$$

Now that we know the orders, the specific rate constant, k , can be evaluated by substituting any of the three sets of data into the rate-law expression. Using the data from experiment 1 gives

$$\begin{aligned} \text{rate}_1 &= k[A]_1^2[B]_1 \quad \text{or} \quad k = \frac{\text{rate}_1}{[A]_1^2[B]_1} \\ k &= \frac{1.5 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}}{(1.0 \times 10^{-2} \text{ M})^2(1.0 \times 10^{-2} \text{ M})} = 1.5 \text{ M}^{-2} \cdot \text{s}^{-1} \end{aligned}$$

At the temperature at which the measurements were made, the rate-law expression for this reaction is

$$\text{rate} = k[A]^2[B] \quad \text{or} \quad \text{rate} = (1.5 \text{ M}^{-2} \cdot \text{s}^{-1}) [A]^2[B]$$

We can check our result by evaluating k from one of the other sets of data.

STOP & THINK

Whenever possible pick two experiments where only one reactant has different initial concentrations. We can calculate the order for this reactant from the effect of the concentration change on the initial rate of reaction.

STOP & THINK

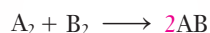
Remember that the specific rate constant k does *not* change with concentration. Only a temperature change or the introduction of a catalyst can change the value of k .

► The units of k depend on the overall order of the reaction, consistent with converting the product of concentrations on the right to concentration/time on the left. For any reaction that is third order overall, the units of k are $\text{M}^{-2} \cdot \text{time}^{-1}$.

Unless otherwise noted, all content on this page is © Cengage Learning.

Problem-Solving Tip Be Sure to Use the Rate of Reaction

The rate-law expression should always give the dependence of the *rate of reaction* on concentrations. The data for the preceding calculation describe the rate of formation of the product C; the coefficient of C in the balanced equation is one, so the rate of reaction is equal to the rate of formation of C. If the coefficient of the measured substance had been 2, then before we began the analysis we should have divided each value of the “initial rate of formation” by 2 to obtain the initial rate of reaction. For instance, suppose we measure the rate of formation of AB in the reaction



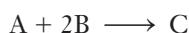
Then

$$\text{rate of reaction} = \frac{1}{2} \left(\frac{\Delta[AB]}{\Delta t} \right) = \frac{1}{2} (\text{rate of formation of AB})$$

Then we would analyze how this reaction rate changes as we change the concentrations of reactants.

An Alternative Method

We can also use a simple algebraic approach to find the exponents in a rate-law expression. Consider a set of rate data similar to that given earlier for the hypothetical reaction



Experiment	Initial [A] (M)	Initial [B] (M)	Initial Rate of Formation of C ($M \cdot s^{-1}$)
1	1.0×10^{-2}	1.0×10^{-2}	1.5×10^{-6}
2	1.0×10^{-2}	2.0×10^{-2}	3.0×10^{-6}
3	2.0×10^{-2}	1.0×10^{-2}	6.0×10^{-6}

Because we are describing the same reaction in each experiment, all the experiments are governed by the same rate-law expression,

$$\text{rate} = k[A]^x[B]^y$$

The initial concentration of A is the same in experiments 1 and 2, so any change in the initial rates for these experiments would be due to different initial concentrations of B. To evaluate y , we solve the ratio of the rate-law expressions of these two experiments for y . We can divide the first rate-law expression by the corresponding terms in the second rate-law expression.

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]_1^x[B]_1^y}{k[A]_2^x[B]_2^y}$$

The value of k always cancels from such a ratio because it is constant at a particular temperature. The initial concentrations of A are equal, so they too cancel. Thus, the expression simplifies to

$$\frac{\text{rate}_1}{\text{rate}_2} = \left(\frac{[B]_1}{[B]_2} \right)^y$$

The only unknown in this equation is y . We substitute data from experiments 1 and 2 into the equation, which gives us

$$\frac{1.5 \times 10^{-6} M \cdot s^{-1}}{3.0 \times 10^{-6} M \cdot s^{-1}} = \left(\frac{1.0 \times 10^{-2} M}{2.0 \times 10^{-2} M} \right)^y$$

$$0.5 = (0.5)^y \quad \text{so} \quad y = 1$$



Charles D. Winters

When heated in air, steel wool glows but does not burn rapidly, due to the low O_2 concentration in air (about 21%). When pure oxygen is passed through the center of the steel wool via a porous tube, the steel wool burns vigorously because of the much greater accessibility of O_2 reactant molecules.

► It does not matter which way we take the ratio. We would get the same value for y if we divided the second rate-law expression by the first—try it!

Thus far, we know that the rate-law expression is

$$\text{rate} = k[\text{A}]^x [\text{B}]^1$$

Next we evaluate x . In experiments 1 and 3, the initial concentration of B is the same, so any change in the initial rates for these experiments would be due to the different initial concentrations of A. We solve the ratio of the rate-law expressions of these two experiments for x . We divide the third rate-law expression by the corresponding terms in the first rate-law expression.

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[\text{A}]_3^x [\text{B}]_3^1}{k[\text{A}]_1^x [\text{B}]_1^1}$$

The value k cancels, and so do the concentrations of B because they are equal. Thus, the expression simplifies to

$$\begin{aligned} \frac{\text{rate}_3}{\text{rate}_1} &= \frac{[\text{A}]_3^x}{[\text{A}]_1^x} = \left(\frac{[\text{A}]_3}{[\text{A}]_1} \right)^x \\ \frac{6.0 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}}{1.5 \times 10^{-6} \text{ M} \cdot \text{s}^{-1}} &= \left(\frac{2.0 \times 10^{-2} \text{ M}}{1.0 \times 10^{-2} \text{ M}} \right)^x \\ 4.0 &= (2.0)^x \quad \text{so} \quad x = 2 \end{aligned}$$

The power to which [A] is raised in the rate-law expression is 2, so the rate-law expression for this reaction is the same as that obtained earlier.

$$\text{rate} = k[\text{A}]^2 [\text{B}]^1 \quad \text{or} \quad \text{rate} = k[\text{A}]^2 [\text{B}]$$

Problem-Solving Tip

Although we will usually work with simple integer values for reactant orders, fractional values can occur. For fractional orders the value cannot be determined quite so simply. In the previous example, if doubling the concentration of [A] changed the rate by a factor of 2.83 we would have:

$$2.83 = (2.0)^x$$

In this case the value of x is not obvious. But we can easily solve for x by taking the log of each side and remembering that the log of A^x is $(x)(\log A)$.

$$\log(2.83) = (x)\log(2.0)$$

Dividing through by $\log(2.0)$ gives

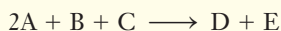
$$x = \log(2.83)/\log(2.0)$$

$$x = 0.452/0.301 = 1.50$$

So in this case the order of [A] is 1.5 or $[\text{A}]^{1.5}$

EXAMPLE 16-3 Method of Initial Rates

Given the following data, determine the rate-law expression and the value of the rate constant for the reaction



Experiment	Initial [A]	Initial [B]	Initial [C]	Initial Rate of Formation of E
1	0.20 M	0.20 M	0.20 M	$2.4 \times 10^{-6} \text{ M} \cdot \text{min}^{-1}$
2	0.40 M	0.30 M	0.20 M	$9.6 \times 10^{-6} \text{ M} \cdot \text{min}^{-1}$
3	0.20 M	0.30 M	0.20 M	$2.4 \times 10^{-6} \text{ M} \cdot \text{min}^{-1}$
4	0.20 M	0.40 M	0.60 M	$7.2 \times 10^{-6} \text{ M} \cdot \text{min}^{-1}$

► The coefficient of E in the balanced equation is 1, so the rate of reaction is equal to the rate of formation of E.

Plan

The rate law is of the form: $\text{rate} = k[\text{A}]^x[\text{B}]^y[\text{C}]^z$. We must evaluate x , y , z , and k . We use the reasoning outlined earlier; in this presentation the first method is used.

Solution

Dependence on [B]: In experiments 1 and 3, the initial concentrations of A and C are unchanged. Thus, any change in the rate would be due to the change in concentration of B. But we see that the rate is the same in experiments 1 and 3, even though the concentration of B is different. Thus, the reaction rate is independent of [B], so $y = 0$ (zero order). We can neglect changes in [B] in subsequent reasoning. The rate law can now be simplified to

$$\text{rate} = k[\text{A}]^x[\text{C}]^z$$

Dependence on [C]: Experiments 1 and 4 involve the same initial concentration of A; thus the observed change in rate must be due entirely to the changed [C]. So we compare experiments 1 and 4 to find z .

$$[\text{C}] \text{ has increased by a factor of } \frac{0.60}{0.20} = 3.0 = [\text{C}] \text{ ratio}$$

The rate changes by a factor of

$$\frac{7.2 \times 10^{-6}}{2.4 \times 10^{-6}} = 3.0 = \text{rate ratio}$$

The exponent z can be deduced from

$$\text{rate ratio} = ([\text{C}] \text{ ratio})^z$$

$$3.0 = (3.0)^z \quad \text{so} \quad z = 1 \quad \text{The reaction is first order in [C].}$$

Now we know that the rate law is of the form

$$\text{rate} = k[\text{A}]^x[\text{C}]$$

Dependence on [A]: We use experiments 1 and 2 to evaluate x , because [A] is changed, [B] does not matter, and [C] is unaltered. The observed rate change is due *only* to the changed [A].

$$[\text{A}] \text{ has increased by a factor of } \frac{0.40}{0.20} = 2.0 = [\text{A}] \text{ ratio}$$

The rate increases by a factor of

$$\frac{9.6 \times 10^{-6}}{2.4 \times 10^{-6}} = 4.0 = \text{rate ratio}$$

The exponent x can be deduced from

$$\text{rate ratio} = ([\text{A}] \text{ ratio})^x$$

$$4.0 = (2.0)^x \quad \text{so} \quad x = 2 \quad \text{The reaction is second order in [A].}$$

From these results we can write the complete rate-law expression.

$$\text{rate} = k[\text{A}]^2[\text{B}]^0[\text{C}]^1 \quad \text{or} \quad \text{rate} = k[\text{A}]^2[\text{C}]$$

We can evaluate the specific rate constant, k , by substituting any of the four sets of data into the rate-law expression we have just derived. Data from experiment 2 give

$$k = \frac{\text{rate}_2}{[\text{A}]_2^2[\text{C}]_2} = \frac{9.6 \times 10^{-6} \text{ M} \cdot \text{min}^{-1}}{(0.40 \text{ M})^2(0.20 \text{ M})} = 3.0 \times 10^{-4} \text{ M}^{-2} \cdot \text{min}^{-1}$$

The rate-law expression can also be written with the value of k incorporated.

$$\text{rate} = (3.0 \times 10^{-4} \text{ M}^{-2} \cdot \text{min}^{-1}) [\text{A}]^2[\text{C}]$$

This expression allows us to calculate the rate at which this reaction occurs with any known concentrations of A and C (provided some B is present). As we shall see presently, changes in temperature alter reaction rates. This value of k is valid *only* at the temperature at which the data were collected.

You should now work Exercises 17 and 18.

► The alternative algebraic method outlined previously can also be used.

► $[\text{B}]^0 = 1$

► It is helpful to set up the ratios with the larger concentration on top to give a ratio > 1 .

STOP & THINK

Because we are comparing only the rate change due to concentration changes in A, the coefficient of 2 for reactant A cancels out in the ratio, so it does not play a role here.

Problem-Solving Tip Check the Rate Law You Have Derived

If the rate law that you deduce from initial rate data is correct, it will not matter which set of data you use to calculate k . As a check, you can calculate k several times, once from each set of experimental concentration and rate data. If the reaction orders in your derived rate law are correct, then all sets of experimental data will give the same value of k (within rounding error); but if the orders are wrong, then the k values will vary considerably.

EXAMPLE 16-4 Method of Initial Rates

Use the following initial rate data to determine the form of the rate-law expression for the reaction



Experiment	Initial [A]	Initial [B]	Initial Rate of Formation of D
1	$1.00 \times 10^{-2} M$	$1.00 \times 10^{-2} M$	$6.00 \times 10^{-3} M \cdot \text{min}^{-1}$
2	$2.00 \times 10^{-2} M$	$3.00 \times 10^{-2} M$	$1.44 \times 10^{-1} M \cdot \text{min}^{-1}$
3	$1.00 \times 10^{-2} M$	$2.00 \times 10^{-2} M$	$1.20 \times 10^{-2} M \cdot \text{min}^{-1}$

Plan

The rate law is of the form $\text{rate} = k[A]^x[B]^y$. No two experiments have the same initial [B], so let's use the alternative method presented earlier to evaluate x and y .

Solution

The initial concentration of A is the same in experiments 1 and 3. We divide the third rate-law expression by the corresponding terms in the first one

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[A]_3^x[B]_3^y}{k[A]_1^x[B]_1^y}$$

The initial concentrations of A are equal, so they cancel, as does k . Simplifying and then substituting known values of rates and [B],

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{[B]_3^y}{[B]_1^y} \quad \text{or} \quad \frac{1.20 \times 10^{-2} M \cdot \text{min}}{6.00 \times 10^{-3} M \cdot \text{min}} = \left(\frac{2.00 \times 10^{-2} M}{1.00 \times 10^{-2} M} \right)^y$$

$$2.0 = (2.0)^y \quad \text{or} \quad y = 1 \quad \text{The reaction is first order in [B].}$$

No two of the experimental runs have the same concentrations of B, so we must proceed somewhat differently. Let's compare experiments 1 and 2. The observed change in rate must be due to the *combination* of the changes in [A] and [B]. We can divide the second rate-law expression by the corresponding terms in the first one, cancel the equal k values, and collect terms.

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]_2^x[B]_2^y}{k[A]_1^x[B]_1^y} = \left(\frac{[A]_2}{[A]_1} \right)^x \left(\frac{[B]_2}{[B]_1} \right)^y$$

Now let's insert the known values for rates and concentrations and the known [B] exponent (order) of 1.

$$\frac{1.44 \times 10^{-1} M \cdot \text{min}^{-1}}{6.00 \times 10^{-3} M \cdot \text{min}^{-1}} = \left(\frac{2.00 \times 10^{-2} M}{1.00 \times 10^{-2} M} \right)^x \left(\frac{3.00 \times 10^{-2} M}{1.00 \times 10^{-2} M} \right)^1$$

$$24.0 = (2.00)^x (3.00)$$

$$8.00 = (2.00)^x \quad \text{or} \quad x = 3 \quad \text{The reaction is third order in [A].}$$

The rate-law expression has the form $\text{rate} = k[A]^3[B]$.

You should now work Exercise 22.

► This is solvable because we have already determined the order of B.

16-4 Concentration Versus Time: The Integrated Rate Equation

Often we want to know the concentration of a reactant that would remain after some specified time, or how long it would take for some amount of the reactants to be used up.

The equation that relates *concentration* and *time* is the **integrated rate equation**. We can also use it to calculate the **half-life**, $t_{1/2}$, of a reactant—the time it takes for half of that reactant to be converted into product. The integrated rate equation and the half-life are different for reactions of different order.

We will look at relationships for some simple cases. If you know calculus, you may be interested in the derivation of the integrated rate equations. This development is presented in the Enrichments at the end of this section.

First-Order Reactions

For reactions involving $aA \longrightarrow$ products that are *first order in A* and *first order overall*, the integrated rate equation is

$$\ln \left(\frac{[A]_0}{[A]} \right) = akt \quad (\text{first order})$$

$[A]_0$ is the initial concentration of reactant A, and $[A]$ is its concentration at some time, t , after the reaction begins. Solving this relationship for t gives

$$t = \frac{1}{ak} \ln \left(\frac{[A]_0}{[A]} \right)$$

By definition, $[A] = \frac{1}{2}[A]_0$ at $t = t_{1/2}$. Thus

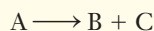
$$t_{1/2} = \frac{1}{ak} \ln \frac{[A]_0}{\frac{1}{2}[A]_0} = \frac{1}{ak} \ln 2$$

$$t_{1/2} = \frac{\ln 2}{ak} = \frac{0.693}{ak} \quad (\text{first order})$$

This relates the half-life of a reactant in a *first-order reaction* and its rate constant, k . In such reactions, the half-life *does not depend* on the initial concentration of A. This is not true for reactions having overall orders other than first order.

EXAMPLE 16-5 Half-Life: First-Order Reaction

Compound A decomposes to form B and C in a reaction that is first order with respect to A and first order overall. At 25°C, the specific rate constant for the reaction is 0.0450 s^{-1} . What is the half-life of A at 25°C?



Plan

We use the equation given earlier for $t_{1/2}$ for a first-order reaction. The value of k is given in the problem; the coefficient of reactant A is $a = 1$.

Solution

$$t_{1/2} = \frac{\ln 2}{ak} = \frac{0.693}{1(0.0450 \text{ s}^{-1})} = 15.4 \text{ s}$$

After 15.4 seconds of reaction, half of the original reactant remains, so $[A] = \frac{1}{2}[A]_0$.

You should now work Exercise 37.

► The variable a represents the coefficient of reactant A in the balanced overall equation.

► When time $t_{1/2}$ has elapsed, half of the original $[A]_0$ has reacted, so half of it remains.

► Nuclear decay (Chapter 22) is a very important first-order process. Exercises at the end of that chapter involve calculations of nuclear decay rates.

STOP & THINK

Many examples, especially those involving rates of radioactive decay, have coefficients of 1. Some textbooks do not show a in the rate expression for first order. It is presumed to be one unless stated otherwise.



Problem-Solving Tip

If the problem you are solving asks for or gives *time*, use the integrated rate equation. If it asks for or gives *rate*, use the rate-law expression.

EXAMPLE 16-6 Concentration Versus Time: First-Order Reaction

The reaction $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g})$ obeys the rate law: $\text{rate} = k[\text{N}_2\text{O}_5]$, in which the specific rate constant is 0.00840 s^{-1} at a certain temperature. (a) If 2.50 moles of N_2O_5 were placed in a 5.00-liter container at that temperature, how many moles of N_2O_5 would remain after 1.00 minute? (b) How long would it take for 90% of the original N_2O_5 to react?

Plan

We apply the integrated first-order rate equation.

$$\ln \left(\frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]} \right) = akt$$

(a) First, we must determine $[\text{N}_2\text{O}_5]_0$, the original molar concentration of N_2O_5 . Then we solve for $[\text{N}_2\text{O}_5]$, the molar concentration after 1.00 minute. We must remember to express k and t using the same time units. Finally, we convert molar concentration of N_2O_5 to moles remaining. (b) We solve the integrated first-order equation for the required time.

Solution

(a) The original concentration of N_2O_5 is

$$[\text{N}_2\text{O}_5]_0 = \frac{2.50 \text{ mol}}{5.00 \text{ L}} = 0.500 \text{ M}$$

The other quantities are

$$a = 2 \quad k = 0.00840 \text{ s}^{-1} \quad t = 1.00 \text{ min} = 60.0 \text{ s} \quad [\text{N}_2\text{O}_5] = ?$$

The only unknown in the integrated rate equation is $[\text{N}_2\text{O}_5]$ after 1.00 minute. Let us solve for the unknown. Because $\ln x/y = \ln x - \ln y$,

$$\begin{aligned} \ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]} &= \ln [\text{N}_2\text{O}_5]_0 - \ln [\text{N}_2\text{O}_5] = akt \\ \ln [\text{N}_2\text{O}_5] &= \ln [\text{N}_2\text{O}_5]_0 - akt \\ &= \ln (0.500) - (2)(0.00840 \text{ s}^{-1})(60.0 \text{ s}) = -0.693 - 1.008 \\ \ln [\text{N}_2\text{O}_5] &= -1.701 \end{aligned}$$

Taking the inverse natural logarithm of both sides gives

$$[\text{N}_2\text{O}_5] = 1.82 \times 10^{-1} \text{ M}$$

Thus, after 1.00 minute of reaction, the concentration of N_2O_5 is 0.182 M. The number of moles of N_2O_5 left in the 5.00-L container is

$$? \text{ mol N}_2\text{O}_5 = 5.00 \text{ L} \times \frac{0.182 \text{ mol}}{\text{L}} = 0.910 \text{ mol N}_2\text{O}_5$$

(b) Because the integrated *first-order* rate equation involves a *ratio* of concentrations, we do not need to obtain the numerical value of the required concentration. When 90.0% of the original N_2O_5 has reacted, 10.0% remains, or

$$[\text{N}_2\text{O}_5] = (0.100)[\text{N}_2\text{O}_5]_0$$

We make this substitution into the integrated rate equation and solve for the elapsed time, t .

$$\ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]} = akt$$

STOP & THINK

Make sure the units of time are the same—chemists often use seconds (s) in specific rate constants.

► $\text{inv } \ln x = e^{\ln x}$

Be sure that you know how to use your calculator to obtain x by taking the inverse of $\ln x$.

$$\ln \frac{[\text{N}_2\text{O}_5]_0}{(0.100)[\text{N}_2\text{O}_5]_0} = (2)(0.00840 \text{ s}^{-1})t$$

$$\ln(10.0) = (0.0168 \text{ s}^{-1})t$$

$$2.302 = (0.0168 \text{ s}^{-1})t \quad \text{or} \quad t = \frac{2.302}{0.0168 \text{ s}^{-1}} = 137 \text{ seconds}$$

You should now work Exercises 34 and 38.



Problem-Solving Tip Does Your Answer Make Sense?

We know that the amount of N_2O_5 in Example 16-6 must be decreasing. The calculated result, 0.910 mol N_2O_5 after 1.00 minute, is less than the initial amount, 2.50 mol N_2O_5 , which is a reasonable result. If our solution had given a result that was *larger* than the original, we should recognize that we must have made some error. For example, if we had *incorrectly* written the equation as

$$\ln \frac{[\text{N}_2\text{O}_5]}{[\text{N}_2\text{O}_5]_0} = akt$$

we would have obtained $[\text{N}_2\text{O}_5] = 1.37 \text{ M}$, corresponding to 6.85 mol N_2O_5 . This would be more N_2O_5 than was originally present, which we should immediately recognize as an impossible answer.

Second-Order Reactions

For reactions involving $a\text{A} \longrightarrow \text{products}$ that are *second order with respect to A and second order overall*, the integrated rate equation is

$$\frac{1}{[\text{A}]} - \frac{1}{[\text{A}]_0} = akt \quad \left(\begin{array}{l} \text{second order in A,} \\ \text{second order overall} \end{array} \right)$$

For $t = t_{1/2}$, we have $[\text{A}] = \frac{1}{2}[\text{A}]_0$, so

$$\frac{1}{\frac{1}{2}[\text{A}]_0} - \frac{1}{[\text{A}]_0} = akt_{1/2}$$

Simplifying and solving for $t_{1/2}$, we obtain the relationship between the rate constant and $t_{1/2}$.

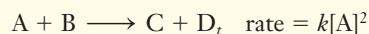
$$t_{1/2} = \frac{1}{ak[\text{A}]_0} \quad \left(\begin{array}{l} \text{second order in A,} \\ \text{second order overall} \end{array} \right)$$

In this case $t_{1/2}$ *depends on the initial concentration of A*. Figure 16-4 illustrates the different behavior of half-life for first- and second-order reactions.

► You should carry out the algebraic steps to solve for $t_{1/2}$.

EXAMPLE 16-7 Half-Life: Second-Order Reaction

Compounds A and B react to form C and D in a reaction that was found to be second order in A and second order overall. The rate constant at 30°C is 0.622 liter per mole per minute. What is the half-life of A when $4.10 \times 10^{-2} \text{ M}$ A is mixed with excess B?



Plan

As long as some B is present, only the concentration of A affects the rate. The reaction is second order in [A] and second order overall, so we use the appropriate equation for the half-life.

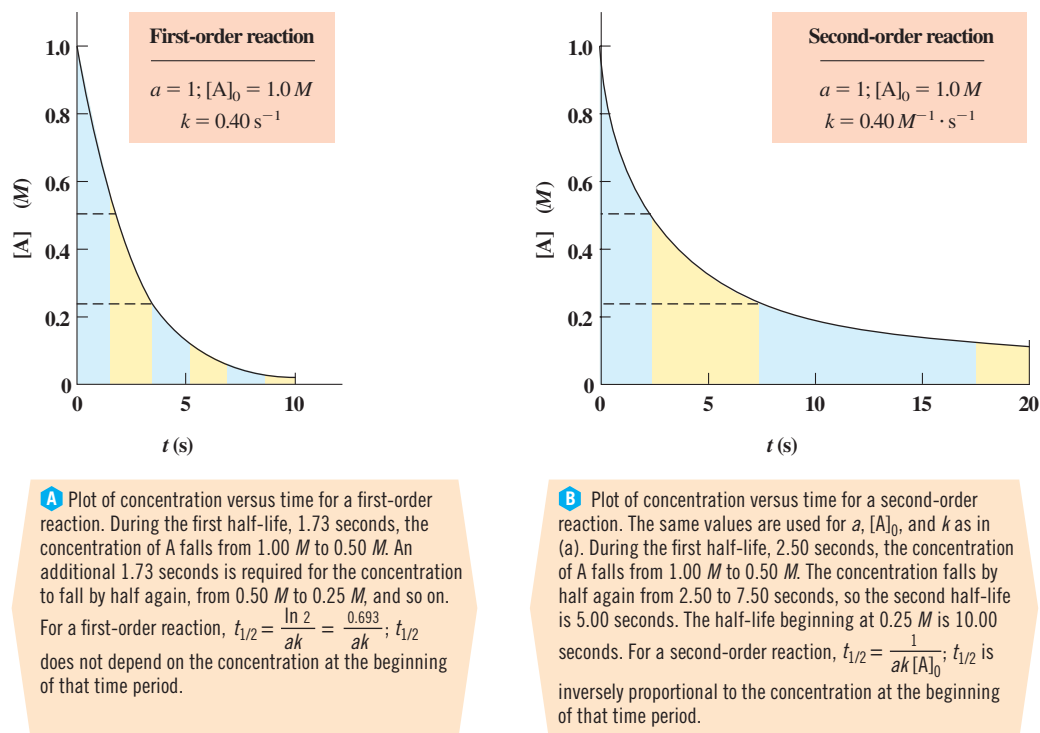


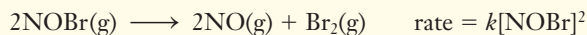
Figure 16-4 Comparison of first and second order decreases in reactant concentration.

Solution

$$t_{1/2} = \frac{1}{ak[A]_0} = \frac{1}{(1)(0.622 \text{ M}^{-1} \cdot \text{min}^{-1})(4.10 \times 10^{-2} \text{ M})} = 39.2 \text{ min}$$

EXAMPLE 16-8 Concentration Versus Time: Second-Order Reaction

The gas-phase decomposition of NOBr is second order in [NOBr], with $k = 0.810 \text{ M}^{-1} \cdot \text{s}^{-1}$ at 10°C. We start with $4.00 \times 10^{-3} \text{ M}$ NOBr in a flask at 10°C. How many seconds does it take to use up $1.50 \times 10^{-3} \text{ M}$ of this NOBr?



Plan

We first determine the concentration of NOBr that remains after $1.50 \times 10^{-3} \text{ M}$ is used up. Then we use the second-order integrated rate equation to determine the time required to reach that concentration.

Solution

$$\underline{?} \text{ M NOBr remaining} = (0.00400 - 0.00150) \text{ M} = 0.00250 \text{ M} = [\text{NOBr}]$$

We solve the integrated rate equation $\frac{1}{[\text{NOBr}]} - \frac{1}{[\text{NOBr}]_0} = akt$ for t .

$$\begin{aligned} t &= \frac{1}{ak} \left(\frac{1}{[\text{NOBr}]} - \frac{1}{[\text{NOBr}]_0} \right) = \frac{1}{(2)(0.810 \text{ M}^{-1} \cdot \text{s}^{-1})} \left(\frac{1}{0.00250 \text{ M}} - \frac{1}{0.00400 \text{ M}} \right) \\ &= \frac{1}{1.62 \text{ M}^{-1} \cdot \text{s}^{-1}} (400 \text{ M}^{-1} - 250 \text{ M}^{-1}) \\ &= 92.6 \text{ s} \end{aligned}$$

You should now work Exercise 32.

► The coefficient of NOBr is $a = 2$.

EXAMPLE 16-9 Concentration Versus Time: Second-Order Reaction

Consider the reaction of Example 16-8 at 10°C. If we start with $2.40 \times 10^{-3} M$ NOBr, what concentration of NOBr will remain after 5.00 minutes of reaction?

Plan

We use the integrated second-order rate equation to solve for the concentration of NOBr remaining at $t = 5.00$ minutes.

Solution

Again, we start with the expression $\frac{1}{[\text{NOBr}]} - \frac{1}{[\text{NOBr}]_0} = akt$. Then we put in the known values and solve for [NOBr].

$$\frac{1}{[\text{NOBr}]} - \frac{1}{2.40 \times 10^{-3} M} = (2) (0.810 M^{-1} \cdot s^{-1}) (5.00 \text{ min}) \left(\frac{60 \text{ s}}{1 \text{ min}} \right)$$

$$\frac{1}{[\text{NOBr}]} - 4.17 \times 10^2 M^{-1} = 486 M^{-1}$$

$$\frac{1}{[\text{NOBr}]} = 486 M^{-1} + 417 M^{-1} = 903 M^{-1}$$

$$[\text{NOBr}] = \frac{1}{903 M^{-1}} = 1.11 \times 10^{-3} M \quad (46.2\% \text{ remains unreacted})$$

Thus, 53.8% of the original concentration of NOBr reacts within the first 5 minutes. This is reasonable because, as you can easily verify, the reaction has an initial half-life of 257 seconds, or 4.29 minutes.

You should now work Exercises 33 and 36.

Zero-Order Reaction

For a reaction $aA \longrightarrow \text{products}$ that is zero order, the reaction rate is independent of concentrations. We can write the rate-law expression as

$$\text{rate} = -\frac{1}{a} \left(\frac{\Delta[A]}{\Delta t} \right) = k$$

The corresponding integrated rate equation is

$$[A] = [A]_0 - akt \quad (\text{zero order})$$

and the half-life is

$$t_{1/2} = \frac{[A]_0}{2ak} \quad (\text{zero order})$$

Table 16-2 summarizes the relationships that we have presented in Sections 16-3 and 16-4.

Table 16-2 Summary of Relationships for Various Orders of the Reaction $aA \rightarrow \text{Products}$

	Order		
	Zero	First	Second
Rate-law expression	rate = k	rate = $k[A]$	rate = $k[A]^2$
Integrated rate equation	$[A] = [A]_0 - akt$	$\ln \frac{[A]_0}{[A]} = akt$	$\frac{1}{[A]} - \frac{1}{[A]_0} = akt$
Half-life, $t_{1/2}$	$\frac{[A]_0}{2ak}$	$\frac{\ln 2}{ak} = \frac{0.693}{ak}$	$\frac{1}{ak[A]_0}$

Problem-Solving Tip Which Equation Should Be Used?

How can you tell which equation to use to solve a particular problem?

1. You must decide whether to use the rate-law expression or the integrated rate equation. Remember that

the *rate-law expression* relates *rate and concentration*

whereas

the *integrated rate equation* relates *time and concentration*.

When you need to find the *rate* that corresponds to particular concentrations, or the concentrations needed to give a desired rate, you should use the rate-law expression. When *time* is involved in the problem, you should use the integrated rate equation.

2. You must choose the form of the rate-law expression or the integrated rate equation—zero, first, or second order—that is appropriate to the order of the reaction. These are summarized in Table 16-2. One of the following usually helps you decide.
 - a. The statement of the problem may state explicitly what the order of the reaction is.
 - b. The rate-law expression may be given so that you can tell the order of the reaction from the exponents in that expression.
 - c. The units of the specific rate constant, k , may be given; you can interpret these stated units to tell you the order of the reaction.

STOP & THINK

Many students do not realize that it is easier to derive the units of the rate constants for zero-, first-, and second-order reactions than it is to memorize them.

Order	Units of k
0	$M \cdot \text{time}^{-1}$
1	time^{-1}
2	$M^{-1} \cdot \text{time}^{-1}$

► You should test this method using the concentration-versus-time data of Example 16-10, plotted in Figure 16-8b.

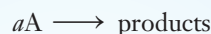
One method of assessing reaction order is based on comparing successive half-lives. As we have seen, $t_{1/2}$ for a first-order reaction does not depend on initial concentration. We can measure the time required for different concentrations of a reactant to fall to half of their original values. If this time remains constant, it is an indication that the reaction is first order for that reactant and first order overall (see Figure 16-4a). By contrast, for other orders of reaction, $t_{1/2}$ would change depending on initial concentration. For a second-order reaction, successively measured $t_{1/2}$ values would increase by a factor of 2 as $[A]_0$ decreases by a factor of 2 (see Figure 16-4b). $[A]_0$ is measured at the *beginning of each particular measurement period*.

ENRICHMENT



Calculus Derivation of Integrated Rate Equations

The derivation of the integrated rate equation is an example of the use of calculus in chemistry. The following derivation is for a reaction that is assumed to be first order in a reactant A and first order overall. If you do not know calculus, you can still use the results of this derivation, as we have already shown in this section. For the reaction



the rate is expressed as

$$\text{rate} = -\frac{1}{a} \left(\frac{\Delta[A]}{\Delta t} \right)$$

For a first-order reaction, the rate is proportional to the first power of [A].

$$-\frac{1}{a} \left(\frac{\Delta[A]}{\Delta t} \right) = k[A]$$

In calculus terms, we express the change during an infinitesimally short time dt as the derivative of [A] with respect to time.

$$-\frac{1}{a} \frac{d[A]}{dt} = k[A]$$

Separating variables, we obtain

$$-\frac{d[A]}{[A]} = (ak)dt$$

We integrate this equation with limits: As the reaction progresses from time = 0 (the start of the reaction) to time = t elapsed, the concentration of A goes from $[A]_0$, its starting value, to [A], the concentration remaining after time t :

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = ak \int_0^t dt$$

The result of the integration is

$$-(\ln[A] - \ln[A]_0) = ak(t - 0) \quad \text{or} \quad \ln[A]_0 - \ln[A] = akt$$

Remembering that $\ln(x) - \ln(y) = \ln(x/y)$, we obtain

$$\ln \frac{[A]_0}{[A]} = akt \quad (\text{first order})$$

This is the integrated rate equation for a reaction that is first order in reactant A and first order overall.

Integrated rate equations can be derived similarly from other simple rate laws. For a reaction $aA \rightarrow \text{products}$ that is second order in reactant A and second order overall, we can write the rate equation as

$$-\frac{d[A]}{a dt} = k[A]^2$$

► $-\frac{1}{a} \left(\frac{\Delta[A]}{\Delta t} \right)$ represents the average rate over a finite time interval

Δt .

$-\frac{1}{a} \left(\frac{d[A]}{dt} \right)$ involves a change over an infinitesimally short time interval dt , so it represents the *instantaneous* rate.

Again, using the methods of calculus, we can separate variables, integrate, and rearrange to obtain the corresponding integrated second-order rate equation.

$$\frac{1}{[A]} - \frac{1}{[A]_0} = akt \quad (\text{second order})$$

For a reaction $aA \longrightarrow \text{products}$ that is zero order overall, we can write the rate equation as

$$-\frac{d[A]}{adt} = k$$

In this case, the calculus derivation already described leads to the integrated zero-order rate equation

$$[A] = [A]_0 - akt \quad (\text{zero order})$$

ENRICHMENT

Using Integrated Rate Equations to Determine Reaction Order

Analysis of the slope and intercept of a straight-line plot can often aid in analyzing data. Recall that the standard equation for a straight line may be written as

$$y = mx + b$$

where y is the variable plotted along the ordinate (vertical axis), x is the variable plotted along the abscissa (horizontal axis), m is the slope of the line, and b is the intercept of the line with the y axis (Figure 16-5).

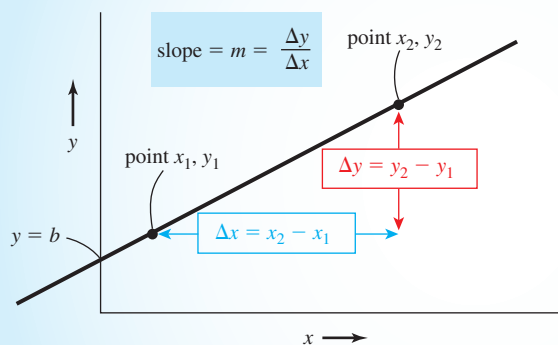


Figure 16-5 Plot of the equation $y = mx + b$, where m and b are constant. The slope of the line (positive in this case) is equal to m ; the intercept on the y axis is equal to b .

We can apply this graphical method to the integrated rate equation to help us determine reaction order from concentration-versus-time data. Let us rearrange the integrated first-order rate equation

$$\ln \frac{[A]_0}{[A]} = akt$$

as follows. The logarithm of a quotient, $\ln (x/y)$, is equal to the difference of the logarithms, $\ln x - \ln y$, so we can write

$$\ln [A]_0 - \ln [A] = akt \quad \text{or} \quad \ln [A] = -akt + \ln [A]_0$$

Comparing this rearranged equation to the standard straight-line equation, we see that $\ln [A]$ can be interpreted as y , and t as x .

$$\underbrace{\ln [A]}_y = \underbrace{-akt}_{m} + \underbrace{\ln [A]_0}_b$$

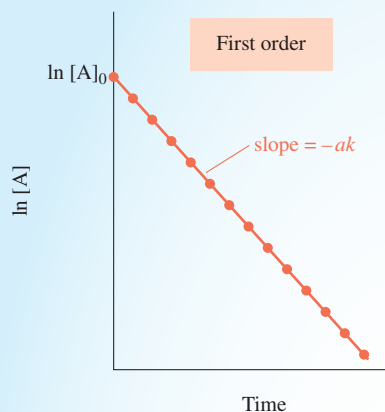


Figure 16-6 Plot of $\ln [A]$ versus time for a reaction $aA \longrightarrow$ products that follows first-order kinetics. The observation that such a plot gives a straight line would confirm that the reaction is first order in $[A]$ and first order overall; that is, $\text{rate} = k[A]$. The slope is equal to $-ak$. Because a and k are positive numbers, the slope of the line is always negative. Logarithms are dimensionless, so the slope has the units $(\text{time})^{-1}$. The logarithm of a quantity less than 1 is negative, so data points for concentrations less than 1 molar would have negative values and appear below the time axis.

The quantity $-ak$ is a constant as the reaction proceeds, so it can be interpreted as m . The initial concentration of A is fixed, so $\ln [A]_0$ is a constant for each experiment, and $\ln [A]_0$ can be interpreted as b . Thus, a plot of $\ln [A]$ versus time for a first-order reaction would be expected to give a straight line (Figure 16-6) with the slope of the line equal to $-ak$ and the intercept equal to $\ln [A]_0$.

We can proceed in a similar fashion with the integrated rate equation for a reaction that is second order in A and second order overall. We rearrange

$$\frac{1}{[A]} - \frac{1}{[A]_0} = akt \quad \text{to read} \quad \frac{1}{[A]} = akt + \frac{1}{[A]_0}$$

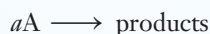
Again comparing this with the equation for a straight line, we see that a plot of $1/[A]$ versus time would be expected to give a straight line (Figure 16-7). The line would have a slope equal to ak and an intercept equal to $1/[A]_0$.

For a zero-order reaction, we can rearrange the integrated rate equation

$$[A]_0 - [A] = akt \quad \text{to} \quad [A] = -akt + [A]_0$$

Comparing this with the equation for a straight line, we see that a straight-line plot would be obtained by plotting concentration versus time, $[A]$ versus t . The slope of this line is $-ak$, and the intercept is $[A]_0$.

This discussion suggests another way to deduce an unknown rate-law expression from experimental concentration data. The following approach is particularly useful for any decomposition reaction, one that involves only one reactant.



We plot the data in various ways as suggested above. *If* the reaction followed zero-order kinetics, *then* a plot of $[A]$ versus t would give a straight line. But *if* the reaction followed first-order kinetics, *then* a plot of $\ln [A]$ versus t would give a straight line whose slope could be interpreted to derive a value of k . *If* the reaction were second order in A and second order overall, *then* neither of these plots would give a straight line, but a plot of $1/[A]$ versus t would. If none of these plots gave a straight line (within expected scatter due to experimental error), we would know that none of these possibilities is the correct order (rate law) for the reaction. Plots to test for other orders can be devised, as can graphical tests for rate-law expressions involving more than one reactant, but those are subjects for more advanced texts. The graphical approach that we have described is illustrated in the following example.

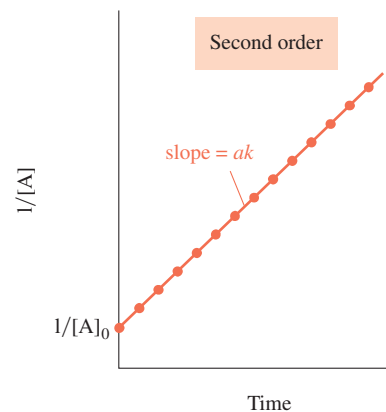


Figure 16-7 Plot of $1/[A]$ versus time for a reaction $aA \longrightarrow$ products that follows second-order kinetics. The observation that such a plot gives a straight line would confirm that the reaction is second order in $[A]$ and second order overall; that is, $\text{rate} = k[A]^2$. The slope is equal to ak . Because a and k are positive numbers, the slope of the line is always positive. Because concentrations cannot be negative, $1/[A]$ is always positive, and the line is always above the time axis.

► It is not possible for *all* of the plots suggested here to yield straight lines for a given reaction. The nonlinearity of the plots may not become obvious, however, if the reaction times used are too short. In practice, all three lines might seem to be straight; we should then suspect that we need to observe the reaction for a longer time.

Time (min)	[A] (mol/L)
0.00	2.000
2.00	1.107
4.00	0.612
6.00	0.338
8.00	0.187
10.00	0.103

EXAMPLE 16-10 Graphical Determination of Reaction Order

We carry out the reaction $A \rightarrow B + C$ at a particular temperature. As the reaction proceeds, we measure the molarity of the reactant, $[A]$, at various times. The observed data are tabulated in the margin. (a) Plot $[A]$ versus time. (b) Plot $\ln [A]$ versus time. (c) Plot $1/[A]$ versus time. (d) What is the order of the reaction? (e) Write the rate-law expression for the reaction. (f) What is the value of k at this temperature?

Plan

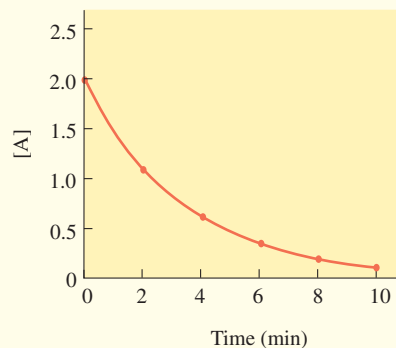
For Parts (a)–(c), we use the observed data to make the required plots, calculating related values as necessary. (d) We can determine the order of the reaction by observing which of these plots gives a straight line. (e) Knowing the order of the reaction, we can write the rate-law expression. (f) The value of k can be determined from the slope of the straight-line plot.

Solution

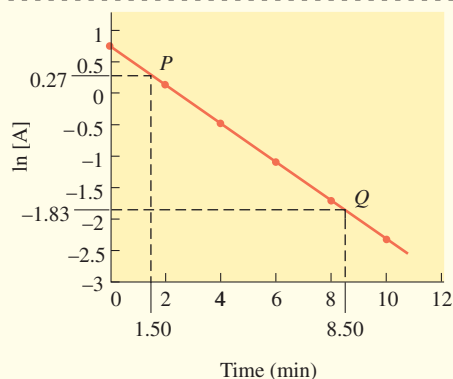
- (a) The plot of $[A]$ versus time is given in Figure 16-8b.
- (b) We first use the given data to calculate the $\ln [A]$ column in Figure 16-8a. These data are then used to plot $\ln [A]$ versus time, as shown in Figure 16-8c.
- (c) The given data are used to calculate the $1/[A]$ column in Figure 16-8a. Then we plot $1/[A]$ versus time, as shown in Figure 16-8d.
- (d) It is clear from the answer to part (b) that the plot of $\ln [A]$ versus time gives a straight line. This tells us that the reaction is first order in $[A]$.
- (e) In the form of a rate-law expression, the answer to part (d) gives $\text{rate} = k[A]$.

Time (min)	[A]	$\ln [A]$	$1/[A]$
0.00	2.000	0.693	0.5000
2.00	1.107	0.102	0.9033
4.00	0.612	-0.491	1.63
6.00	0.338	-1.085	2.95
8.00	0.187	-1.677	5.35
10.00	0.103	-2.273	9.71

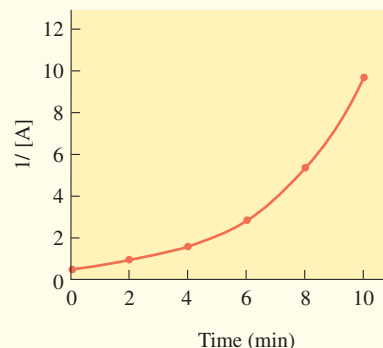
A Data for Example 16-10.



B Example 16-10(a).



C Example 16-10(b).



D Example 16-10(c).

Figure 16-8 Data conversion and plots for Example 16-10. (a) The data are used to calculate the two columns $\ln [A]$ and $1/[A]$. (b) Test for zero-order kinetics: a plot of $[A]$ versus time. The nonlinearity of this plot shows that the reaction does not follow zero-order kinetics. (c) Test for first-order kinetics: a plot of $\ln [A]$ versus time. The observation that this plot gives a straight line indicates that the reaction follows first-order kinetics. (d) Test for second-order kinetics: a plot of $1/[A]$ versus time. If the reaction had followed second-order kinetics, this plot would have resulted in a straight line and the plot in Part (c) would not.

- (f) We use the straight-line plot in Figure 16-8c to find the value of the rate constant for this first-order reaction from the relationship

$$\text{Slope} = -ak \quad \text{or} \quad k = -\frac{\text{slope}}{a}$$

To determine the slope of the straight line, we pick any two points, such as *P* and *Q*, on the line. From their coordinates, we calculate

$$\text{Slope} = \frac{\text{change in ordinate}}{\text{change in abscissa}} = \frac{(-1.83) - (0.27)}{(8.50 - 1.50) \text{ min}} = -0.300 \text{ min}^{-1}$$

$$k = -\frac{\text{slope}}{a} = -\frac{-0.300 \text{ min}^{-1}}{1} = 0.300 \text{ min}^{-1}$$

You should now work Exercises 42 and 43.

The graphical interpretations of concentration-versus-time data for some common reaction orders are summarized in Table 16-3.



Problem-Solving Tip Some Warnings About the Graphical Method for Determining Reaction Order

1. When we deal with real experimental data, there is always some error in each of the data points on the plot. For this reason, we should *not* use experimental data points to determine the slope. (Random experimental errors of only 10% can introduce errors of more than 100% in slopes based on only two points.) Rather we should draw the best straight line and then use points on that line to find its slope. Errors are further minimized by choosing points that are widely separated.
2. Remember that the ordinate is the vertical axis and the abscissa is the horizontal one. If you are not careful to keep the points in the same order in the numerator and denominator, you will get the wrong sign for the slope.

Table 16-3 Graphical Interpretations for Various Orders of the Reaction $aA \longrightarrow \text{Products}$

	Order		
	Zero	First	Second
Plot that gives straight line	$[A]$ vs. t	$\ln [A]$ vs. t	$\frac{1}{[A]}$ vs. t
Direction of straight-line slope	down with time	down with time	up with time
Integrated rate equation	$-ak$	$-ak$	ak
Interpretation of intercept	$[A]_0$	$\ln [A]_0$	$\frac{1}{[A]_0}$

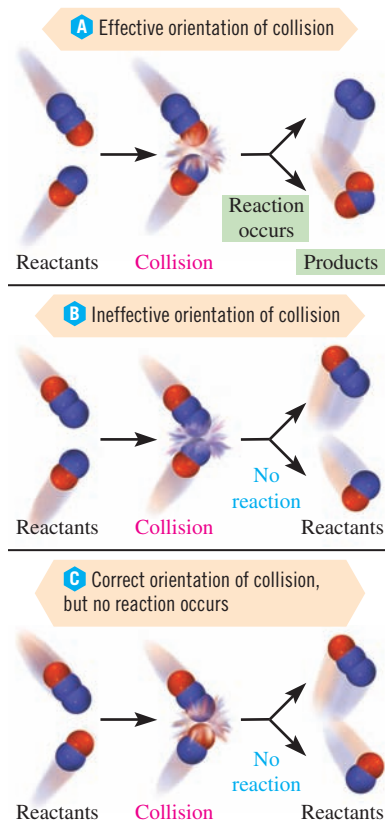
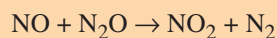


Figure 16-9 Some possible collisions between N_2O and NO molecules in the gas phase. (a) A collision that could be effective in producing the reaction. (b, c) Collisions that would be ineffective. The molecules must have the proper orientations relative to one another *and* have sufficient energy to react.

16-5 Collision Theory of Reaction Rates

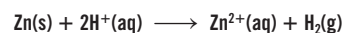
The fundamental notion of the **collision theory of reaction rates** is that for a reaction to occur, molecules, atoms, or ions must first collide. Increased concentrations of reacting species result in greater numbers of collisions per unit time. However, not all collisions result in reaction; that is, not all collisions are **effective collisions**. For a collision to be effective, the reacting species must (1) possess at least a certain minimum energy necessary to rearrange outer electrons in breaking bonds and forming new ones and (2) have the proper orientations toward one another at the time of collision.

Collisions must occur in order for a chemical reaction to proceed, but they do not guarantee that a reaction will occur.

A collision between atoms, molecules, or ions is not like one between two hard billiard balls. Whether or not chemical species “collide” depends on the distance at which they can interact with one another. For instance, the gas-phase ion–molecule reaction $\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3$ can occur with a fairly long-range contact. This is because the interactions between ions and induced dipoles are effective over a relatively long distance. By contrast, the reacting species in the gas reaction $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ are both neutral. They interact appreciably only through very short-range forces between induced dipoles, so they must approach one another very closely before we could say that they “collide.”

Recall (Chapter 12) that the average kinetic energy of a collection of molecules is proportional to the absolute temperature. At higher temperatures, more of the molecules possess sufficient energy to react (see Section 16-8).

The colliding molecules must have the proper orientation relative to one another *and* have sufficient energy to react. If colliding molecules have improper orientations, they do not react even though they may possess sufficient energy. Figure 16-9 depicts some possible collisions between molecules of NO and N_2O , which can react to form NO_2 and N_2 .



Dilute sulfuric acid reacts slowly with zinc metal (*left*), whereas more concentrated acid reacts rapidly (*right*). The $\text{H}^+(\text{aq})$ concentration is higher in the more concentrated acid, so more $\text{H}^+(\text{aq})$ ions collide with Zn per unit time.

Only the collision in Figure 16-9a is in the correct orientation with sufficient kinetic energy to transfer an oxygen atom from the linear N_2O molecule to form the angular NO_2 molecule. For some reactions, the presence of a heterogeneous catalyst (see Section 16-9) can increase the fraction of colliding molecules that have the proper orientations.

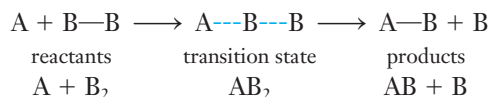
16-6 Transition State Theory

Chemical reactions involve the making and breaking of chemical bonds. The energy associated with a chemical bond is a form of potential energy. Reactions are accompanied by changes in potential energy. Consider the following hypothetical, one-step reaction at a certain temperature.



Figure 16-10 shows plots of potential energy versus the progress of the reaction. In Figure 16-10a the ground state energy of the reactants, A and B₂, is higher than the ground state energy of the products, AB and B. The energy released in the reaction is the difference between these two energies, ΔE . It is related to the change in enthalpy, ΔH_{rxn}^0 (see Section 15-11).

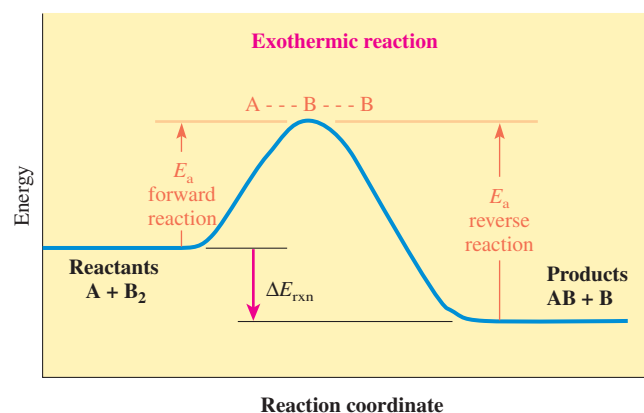
Quite often, for a reaction to occur, some covalent bonds must be broken so that others can be formed. This can occur only if the molecules collide *with enough kinetic energy* to overcome the potential energy stabilization of the bonds. According to the **transition state theory**, the reactants pass through a short-lived, high-energy intermediate state, called a **transition state**, before the products are formed. In the transition state, at least one bond is in the process of being broken while a new bond is being formed. This is represented by dashed lines (or dots) between the atoms.



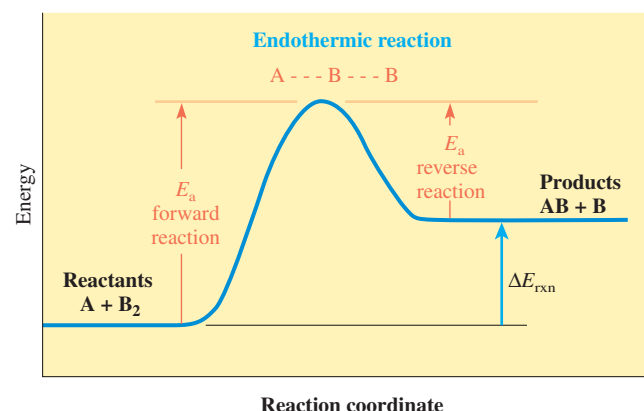
The **activation energy** (or **activation barrier**), E_a , is the kinetic energy that reactant molecules must have to allow them to reach the transition state. If A and B₂ molecules do not possess the necessary amount of energy, E_a , when they collide, a reaction cannot occur. If they do possess sufficient energy to “climb the energy barrier” to reach the transition state, the reaction can proceed. When the atoms go from the transition state arrangement to the product molecules, energy is *released*. If the reaction results in a net *release* of energy (see Figure 16-10a), *more* energy than the activation energy is returned to the surroundings and the reaction is exothermic. If the reaction results in a *net absorption* of energy (see Figure 16-10b), an amount less than E_a is given off when the transition state is converted to products and the reaction is endothermic. The *net* release of energy is ΔE_{rxn} .

For the reverse reaction to occur, some molecules on the right (AB) must have kinetic energy equal to the reverse activation energy, $E_{a \text{ reverse}}$, to allow them to reach the transition state. As you can see from the potential energy diagrams in Figure 16-10,

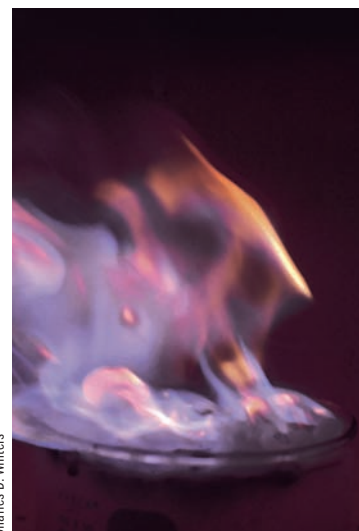
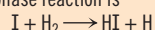
$$E_{a \text{ forward}} - E_{a \text{ reverse}} = \Delta E_{\text{reaction}}$$



A A reaction that releases energy (exothermic). An example of an exothermic gas-phase reaction is



B A reaction that absorbs energy (endothermic). An example of an endothermic gas-phase reaction is



Charles D. Winters

The reaction of potassium metal with water is spontaneous and has a very low activation energy (E_a). The small E_a means that the reaction will be very fast.

► Remember that ΔE_{rxn} relates product energy to reactant energy, regardless of the pathway. ΔE_{rxn} is negative when energy is given off; ΔE_{rxn} is positive when energy is absorbed from the surroundings.

Figure 16-10 A potential energy diagram. The **reaction coordinate** represents how far the reaction has proceeded *along the pathway* leading from reactants to products. This represents the progress of the reaction.

Unless otherwise noted, all content on this page is © Cengage Learning.

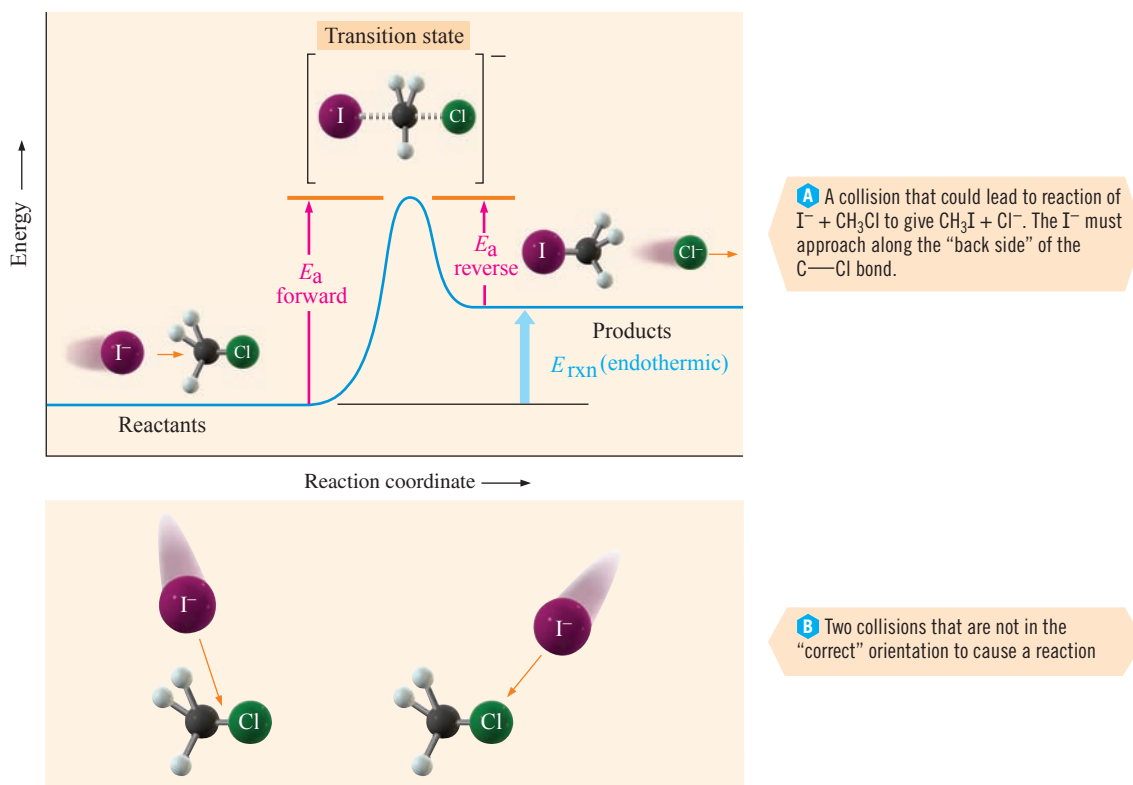


Figure 16-11

► The CH_3Cl and CH_3I molecules each have tetrahedral molecular geometry.

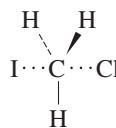
As we shall see, increasing the temperature changes the rate by altering the fraction of molecules that can get over a given energy barrier (see Section 16-8). Introducing a catalyst increases the rate by providing a different pathway that has a lower activation energy (see Section 16-9).

As a specific example that illustrates the ideas of collision theory and transition state theory, consider the reaction of iodide ions with methyl chloride.



Many studies have established that this reaction proceeds as shown in Figure 16-11a. The I^- ion must approach the CH_3Cl molecule from the "back side" of the C—Cl bond, through the middle of the three hydrogen atoms. A collision of an I^- ion with a CH_3Cl molecule from any other direction would not lead to reaction. But a sufficiently energetic collision with the appropriate orientation could allow the new I—C bond to form at the same time that the C—Cl bond is breaking. This collection of atoms, which we represent as

► We can view this transition state as though carbon is only partially bonded to I and only partially bonded to Cl. Because we are showing the molecular geometry using wedges, dashes, and regular lines, the bonds that are forming and breaking are indicated by dotted lines and are in the plane of the paper.



is what we call the transition state of this reaction (see Figure 16-11a). From this state, either of two things could happen: (1) the I—C bond could finish forming and the C—Cl bond could finish breaking with Cl^- leaving, leading to products, or (2) the I—C bond could fall apart with I^- leaving and the C—Cl bond re-forming, leading back to reactants.

16-7 Reaction Mechanisms and the Rate-Law Expression

Some reactions take place in a single step, but most reactions occur in a series of **elementary** or **fundamental steps**. The step-by-step pathway by which a reaction occurs is called the **reaction mechanism**.

The reaction orders for *any single elementary step* are equal to the coefficients for that step.

In many mechanisms, however, one step is much slower than the others.

An overall reaction can never occur faster than its slowest elementary reaction step.

This slowest step is called the **rate-determining step**. The speed at which the slowest step occurs limits the rate at which the overall reaction occurs.

As an analogy, suppose you often drive a distance of 120 miles at the speed limit of 60 mi/h, requiring 2 hours. But one day there is an accident along the route, causing a slow-down. After passing the accident scene, you resume the posted speed of 60 mi/h. If the total time for this trip was 4 hours, then the *average* speed would be only 120 miles/4 hours, or 30 mi/h. Even though you drove for many miles at the same high speed, 60 mi/h, the overall rate was limited by the slow step, passing the accident scene.

The balanced equation for the overall reaction is equal to the sum of *all* the individual fundamental steps, including any that might follow the rate-determining step. We emphasize again that the rate-law exponents *do not necessarily match* the coefficients of the *overall* balanced equation.

For the general overall reaction



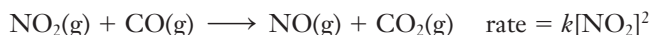
the experimentally determined rate-law expression has the form

$$\text{rate} = k[A]^x[B]^y$$

The values of x and y are related to the coefficients of the reactants in the slowest (rate-determining) step, influenced in some cases by earlier reaction steps.

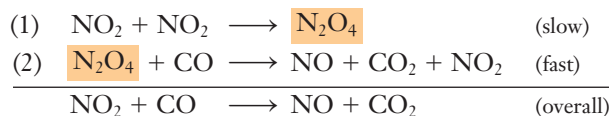
Using a combination of experimental data and chemical intuition, we can *postulate* a mechanism by which a reaction could occur. We can never prove that a proposed mechanism is correct. All we can do is postulate a mechanism that is *consistent* with experimental data. We might later detect reaction-intermediate species that are not explained by the proposed mechanism. We must then modify the mechanism or discard it and propose a new one.

As an example, the reaction of nitrogen dioxide and carbon monoxide has been found to be second order with respect to NO_2 and zero order with respect to CO below 225°C .



The balanced equation for the overall reaction shows the stoichiometry but *does not necessarily mean* that the reaction simply occurs by one molecule of NO_2 colliding with one molecule of CO . If the reaction really took place in that one step, then the rate would be first order in NO_2 and first order in CO , or $\text{rate} = k[\text{NO}_2][\text{CO}]$. The fact that the experimentally determined orders do not match the coefficients in the overall balanced equation tells us that *the reaction does not take place in one step*.

The following proposed two-step mechanism is consistent with the observed rate-law expression.



The rate-determining step of this mechanism involves a *bimolecular* collision between two NO_2 molecules. This is consistent with the rate expression involving $[\text{NO}_2]^2$. Because the CO is involved only after the slow step has occurred, the reaction rate would not depend on $[\text{CO}]$ (i.e., the reaction would be zero order in CO) if this were the actual mechanism.

STOP & THINK

A fundamental reaction step can often look similar to an overall balanced reaction equation, so they are not easy to distinguish. In general, you will be told if a given reaction is fundamental or elementary in nature. If you are not told that a reaction is a fundamental step, you need to be given additional experimental information in order to determine the kinetic orders.

STOP & THINK

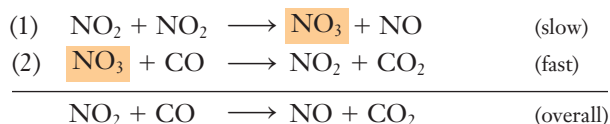
The *rate* of a reaction involves only the steps up to and including the rate-determining step. The *overall stoichiometry* includes all steps in a reaction.

► For clarity, reaction intermediates are shown on an orange background.

► Some reaction intermediates are so unstable that it is very difficult to prove experimentally that they exist.

In this proposed mechanism, N_2O_4 is formed in one step and is completely consumed in a later step. Such a species is called a **reaction intermediate**.

In other studies of this reaction, however, nitrogen trioxide, NO_3 , has been detected as a transient (short-lived) intermediate. The mechanism now thought to be correct is



In this proposed mechanism, two molecules of NO_2 collide to produce one molecule each of NO_3 and NO . The reaction intermediate NO_3 then collides with one molecule of CO and reacts very rapidly to produce one molecule each of NO_2 and CO_2 . Even though two NO_2 molecules are consumed in the first step, one is produced in the second step. The net result is that only one NO_2 molecule is consumed in the overall reaction.

Each of these proposed mechanisms meets both criteria for a plausible mechanism:

(1) The steps add to give the equation for the overall reaction, and (2) the mechanism is consistent with the experimentally determined rate-law expression (in that two NO_2 molecules and no CO molecules are reactants in the slowest reaction step). The NO_3 that has been detected is evidence in favor of the second mechanism, but this does not unequivocally prove that mechanism; it may be possible to think of other mechanisms that would involve NO_3 as an intermediate and would also be consistent with the observed rate law.

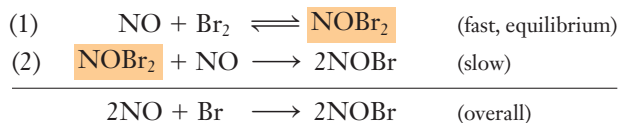
You should be able to distinguish among various species that can appear in a reaction mechanism. So far, we have seen three kinds of species:

1. **Reactant:** More is consumed than is formed.
2. **Product:** More is formed than is consumed.
3. **Reaction intermediate:** Formed in earlier steps, then consumed in an equal amount in later steps.

The gas-phase reaction of NO and Br_2 is known to be second order in NO and first order in Br_2 .



A one-step collision involving two NO molecules and one Br_2 molecule would be consistent with the experimentally determined rate-law expression. However, the likelihood of all three molecules colliding simultaneously is far less than the likelihood of two colliding. *Routes involving only bimolecular collisions or unimolecular decompositions are thought to be far more favorable in reaction mechanisms.* The mechanism is believed to be



The first step involves the collision of one NO molecule (reactant) and one Br_2 molecule (reactant) to produce the intermediate species NOBr_2 . The NOBr_2 can react rapidly, however, to re-form NO and Br_2 . We say that this is an *equilibrium step*. Eventually another NO molecule (reactant) can collide with a short-lived NOBr_2 molecule and react to produce two NOBr molecules (product).

To analyze the rate law that would be consistent with this proposed mechanism, we again start with the slow (rate-determining) Step 2. Denoting the rate constant for this step as k_2 , we could express the rate of this step as

$$\text{rate} = k_2[\text{NOBr}_2][\text{NO}]$$

However, NOBr_2 is a reaction intermediate, so its concentration at the beginning of the second step may not be easy to measure directly. Because NOBr_2 is formed in a fast equilibrium step, we can relate its concentration to the concentrations of the original

► Nonproductive side reactions can produce observable intermediates (such as NO_3) that may not be part of the overall reaction to make products. This is one of the factors that can make kinetics very complicated.

► Think how unlikely it is for three moving billiard balls to collide simultaneously.

► Any fast step that precedes a slow step reaches equilibrium.

STOP & THINK

The rate-law expression of Step 2 (the rate-determining step) determines the rate law for the overall reaction. The overall rate law must not include the concentrations of any intermediate species formed in elementary reaction steps.

reactants. When a reaction or reaction step is at *equilibrium*, its forward (f) and reverse (r) rates are equal.

$$\text{rate}_{\text{if}} = \text{rate}_{\text{ir}}$$

Because this is an elementary step, we can write the rate expression for both directions from the equation for the elementary step

$$k_{\text{if}}[\text{NO}][\text{Br}_2] = k_{\text{ir}}[\text{NOBr}_2]$$

and then rearrange for $[\text{NOBr}_2]$.

$$[\text{NOBr}_2] = \frac{k_{\text{if}}}{k_{\text{ir}}}[\text{NO}][\text{Br}_2]$$

When we substitute the right side of this equation for $[\text{NOBr}_2]$ in the rate expression for the rate-determining step, $\text{rate} = k_2[\text{NOBr}_2][\text{NO}]$, we arrive at the experimentally determined rate-law expression.

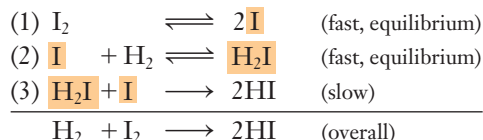
$$\text{rate} = k_2 \left(\frac{k_{\text{if}}}{k_{\text{ir}}} [\text{NO}][\text{Br}_2] \right) [\text{NO}] \quad \text{or} \quad \text{rate} = k[\text{NO}]^2[\text{Br}_2]$$

Similar interpretations apply to most other overall third- or higher-order reactions, as well as many lower-order reactions. When several steps are about equally slow, however, the analysis of experimental data is more complex. Fractional or negative reaction orders can result from complex multistep mechanisms.

One of the earliest kinetic studies involved the gas-phase reaction of hydrogen and iodine to form hydrogen iodide. The reaction was found to be first order in both hydrogen and iodine.



The mechanism that was accepted for many years involved the collision of single molecules of H_2 and I_2 in a simple one-step reaction. Current evidence indicates a more complex process, however. Most kineticists now accept the following mechanism.



In this case neither original reactant appears in the rate-determining step, but both appear in the rate-law expression. Each step is a fundamental reaction in itself. Transition state theory tells us that each step has its own activation energy. Because Step 3 is the slowest, we know that its activation energy is the highest, as shown in Figure 16-12.

In summary,

the experimentally determined reaction orders of reactants indicate the number of molecules of those reactants involved in (1) the slow step only, if it occurs first, or (2) the slow step *and* any fast equilibrium steps preceding the slow step.

► In a mechanism, each individual reaction step is a fundamental step.

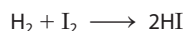
► The product and quotient of constants k_2 , k_{if} , and k_{ir} is another constant, k .

► Apply the algebraic approach described earlier to show that this mechanism is consistent with the observed rate-law expression.

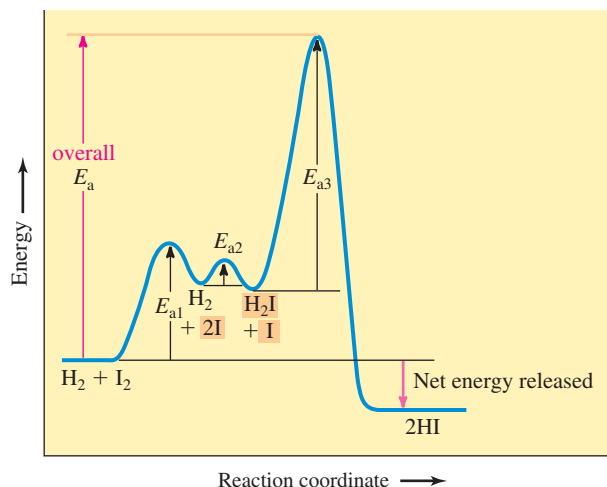
16-8 Temperature: The Arrhenius Equation

The average kinetic energy of a collection of molecules is proportional to the absolute temperature. At a particular temperature, T_1 , a definite fraction of the reactant molecules have sufficient kinetic energy, $\text{KE} > E_a$, to react to form product molecules on collision. At a higher temperature, T_2 , a greater fraction of the molecules possess the necessary activation energy, and the reaction proceeds at a faster rate. This is depicted in Figure 16-13a.

Figure 16-12 A graphical representation of the relative energies of activation for a postulated mechanism for the gas-phase reaction



Reaction intermediates are shown on an orange background.



From experimental observations, Svante Arrhenius developed the mathematical relationship among activation energy, absolute temperature, and the specific rate constant of a reaction, k , at that temperature. The relationship, called the **Arrhenius equation**, is

► Recall that $e = 2.718$ is the base of natural logarithms ($\ln$).

$$k = Ae^{-E_a/RT}$$

or, in logarithmic form,

$$\ln k = \ln A - \frac{E_a}{RT}$$

In this expression, A is a constant having the same units as the rate constant. It is equal to the fraction of collisions with the proper orientations when all reactant concentrations are one molar. R is the universal gas constant, expressed with the same energy units in its numerator as are used for E_a . For instance, when E_a is known in J/mol, the value $R = 8.314 \text{ J/mol} \cdot \text{K}$ is appropriate. Here the unit “mol” is interpreted as “mole of reaction,” as described in Chapter 15. One important point is the following: The greater the value of E_a , the smaller the value of k and the slower the reaction rate (other factors being equal). This is because fewer collisions take place with sufficient energy to get over a high-energy barrier (see Figure 16-13b).

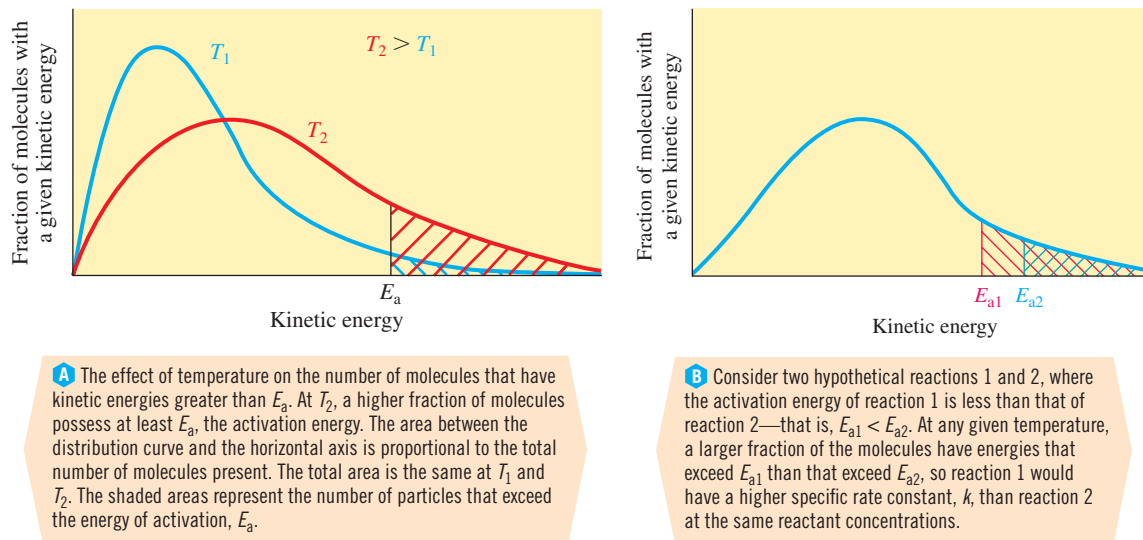


Figure 16-13 Maxwell-Boltzmann distributions, shown here plotted in terms of kinetic energy. Such plots were introduced in Figure 12-9, where they were presented in terms of molecular speed.



Antimony powder reacts with bromine more rapidly at 75°C (left) than at 25°C (right).

The Arrhenius equation predicts that increasing T results in a faster reaction for the same E_a and concentrations.

If T increases $\Rightarrow$ E_a/RT decreases $\Rightarrow$ $-E_a/RT$ increases $\Rightarrow$ $e^{-E_a/RT}$ increases $\Rightarrow$ k increases $\Rightarrow$ **Reaction speeds up**

Let's look at how the rate constant varies with temperature for a given single reaction. Assume that the activation energy and the factor A do not vary with temperature. We can write the Arrhenius equation for two different temperatures. Then we subtract one equation from the other and rearrange the result to obtain

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

The advantage of setting up the equation this way is that the usually unknown A value is cancelled out, making it easier to solve for one of the other values.

Let's substitute some typical values into this equation. The activation energy for many reactions that occur near room temperature is about 50 kJ/mol. For such a reaction, a temperature increase from 300 K to 310 K would result in

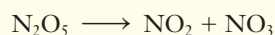
$$\ln \frac{k_2}{k_1} = \frac{50,000 \text{ J/mol}}{(8.314 \text{ J/mol} \cdot \text{K})} \left(\frac{1}{300 \text{ K}} - \frac{1}{310 \text{ K}} \right) = 0.647$$

$$\frac{k_2}{k_1} = 1.91 \approx 2$$

Chemists sometimes use the rule of thumb that near room temperature the rate of a reaction approximately doubles with a 10°C rise in temperature. Such a “rule” must be used with care, however, because it obviously depends on the activation energy.

EXAMPLE 16-11 Arrhenius Equation

The specific rate constant, k , for the following first-order reaction is $9.16 \times 10^{-3} \text{ s}^{-1}$ at 0.0°C. The activation energy of this reaction is 88.0 kJ/mol. Determine the value of k at 2.0°C.



Plan

First we tabulate the values, remembering to convert temperature to the Kelvin scale.

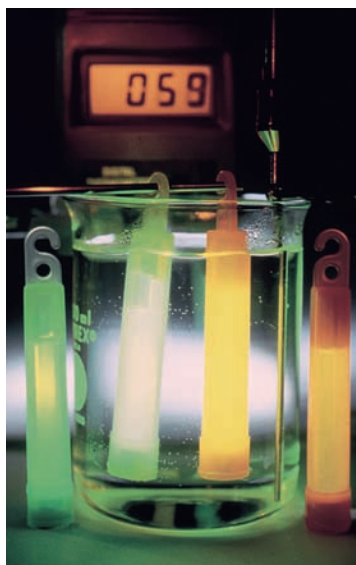
$E_a = 88,000 \text{ J/mol}$		$R = 8.314 \text{ J/mol} \cdot \text{K}$
$k_1 = 9.16 \times 10^{-3} \text{ s}^{-1}$	at	$T_1 = 0.0^\circ\text{C} + 273 = 273 \text{ K}$
$k_2 = ?$	at	$T_2 = 2.0^\circ\text{C} + 273 = 275 \text{ K}$



A fever is your body's natural way of speeding up the immune system (and the rest of your metabolism) to more effectively fight an infection. Part of the old saying “feed a fever” makes a lot of sense from a kinetics viewpoint. Why—in terms of what you have learned in this chapter?



Charles D. Winters



Charles D. Winters

The reaction rate of chemiluminescent light sticks is strongly affected by temperature. In the top photo, the light sticks immersed in cold water (0.2°C) barely glow relative to those sitting outside the beaker at room temperature (22°C). In the bottom photo, the light sticks in the beaker are at 59°C and glow very brightly compared to the room temperature sticks. The light sticks at 59°C will “burn out,” that is, the reactants that produce the light will be consumed much sooner due to the faster reaction at the higher temperature.

STOP & THINK

Remember to convert the answer from J/mol to kJ/mol because E_a values are usually listed in units of kJ/mol.

We use these values in the “two-temperature” form of the Arrhenius equation.

Solution

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \left(\frac{k}{9.16 \times 10^{-3} \text{ s}^{-1}} \right) = \frac{88,000 \text{ J/mol}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{273 \text{ K}} - \frac{1}{275 \text{ K}} \right) = 0.282$$

We can take inverse (natural) logarithms of both sides.

$$e^{\left[\ln \left(\frac{k_2}{9.16 \times 10^{-3} \text{ s}^{-1}} \right) \right]} = e^{0.282}$$

$$\frac{k_2}{9.16 \times 10^{-3} \text{ s}^{-1}} = 1.32$$

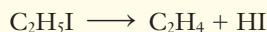
$$k_2 = 1.32(9.16 \times 10^{-3} \text{ s}^{-1}) = 1.21 \times 10^{-2} \text{ s}^{-1}$$

We see that a very small temperature difference, only 2°C, causes an increase in the rate constant (and hence in the reaction rate for the same concentrations) of about 32%. Such sensitivity of rate to temperature change makes the control and measurement of temperature extremely important in chemical reactions.

You should now work Exercise 55.

EXAMPLE 16-12 Activation Energy

The gas-phase decomposition of ethyl iodide to give ethylene and hydrogen iodide is a first-order reaction.



At 600. K, the value of k is $1.60 \times 10^{-5} \text{ s}^{-1}$. When the temperature is raised to 700. K, the value of k increases to $6.36 \times 10^{-3} \text{ s}^{-1}$. What is the activation energy for this reaction?

Plan

We know k at two different temperatures. We solve the two-temperature form of the Arrhenius equation for E_a and evaluate.

Solution

$$k_1 = 1.60 \times 10^{-5} \text{ s}^{-1} \text{ at } T_1 = 600. \text{ K} \quad k_2 = 6.36 \times 10^{-3} \text{ s}^{-1} \text{ at } T_2 = 700. \text{ K}$$

$$R = 8.314 \text{ J/mol} \cdot \text{K} \quad E_a = ?$$

We arrange the Arrhenius equation for E_a .

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{so} \quad E_a = \frac{R \ln \frac{k_2}{k_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

Substituting,

$$E_a = \frac{\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \ln \left(\frac{6.36 \times 10^{-3} \text{ s}^{-1}}{1.60 \times 10^{-5} \text{ s}^{-1}} \right)}{\left(\frac{1}{600. \text{ K}} - \frac{1}{700. \text{ K}} \right)} = \frac{\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (5.98)}{2.38 \times 10^{-4} \text{ K}^{-1}} = \frac{2.09 \times 10^5 \text{ J/mol}}{\text{or } 209 \text{ kJ/mol}}$$

You should now work Exercise 56.

The determination of E_a in the manner illustrated in Example 16-12 may be subject to considerable error because it depends on the measurement of k at only two temperatures. Any error in either of these k values would greatly affect the resulting value of E_a . A more reliable method that uses many measured values for the same reaction is based on a graphical approach. Let us rearrange the single-temperature logarithmic form of the Arrhenius equation and compare it with the equation for a straight line.

$$\underbrace{\ln k}_{y} = - \underbrace{\left(\frac{E_a}{R}\right)}_m \underbrace{\left(\frac{1}{T}\right)}_x + \underbrace{\ln A}_b$$

The value of the collision frequency factor, A , is very nearly constant over moderate temperature changes. Thus, $\ln A$ can be interpreted as the constant term in the equation (the intercept). The slope of the straight line obtained by plotting $\ln k$ versus $1/T$ equals $-E_a/R$. This allows us to determine the value of the activation energy from the slope (Figure 16-14). Exercises 59 and 60 use this method.

► Compare this approach to that described in the earlier Enrichment section for determining k .

16-9 Catalysts

Catalysts are substances that can be added to reaction mixtures to increase the rate of reaction. They provide alternative pathways that increase reaction rates by lowering activation energies.

The activation energy is lowered in all catalyzed reactions, as depicted in Figures 16-15 and 16-16. A catalyst does become involved in the reaction, and although it may be transformed via reaction steps during the catalysis, the starting catalyst is regenerated as the reaction

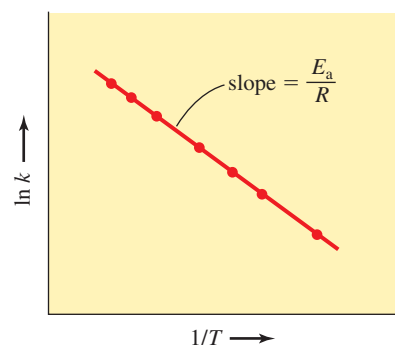


Figure 16-14 A graphical method for determining activation energy, E_a . At each of several different temperatures, the rate constant, k , is determined by methods such as those in Sections 16-3 and 16-4. A plot of $\ln k$ versus $1/T$ gives a straight line with negative slope. The slope of this straight line is $-E_a/R$. Use of this graphical method is often desirable because it partially compensates for experimental errors in individual k and T values.

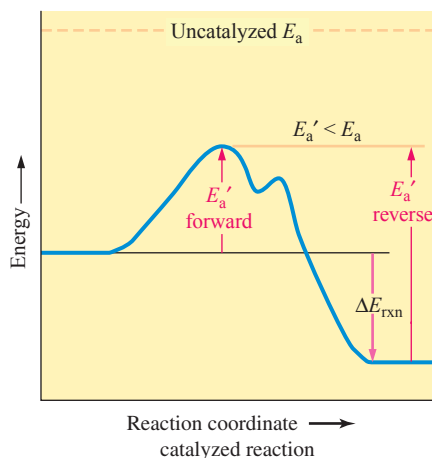
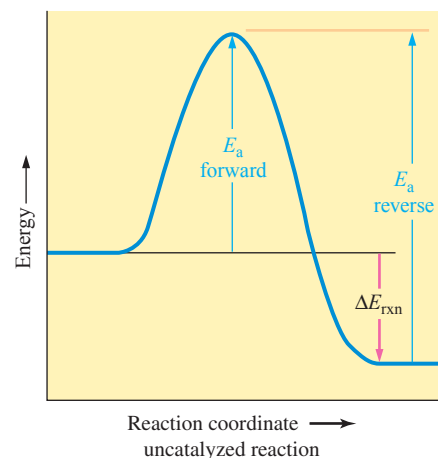


Figure 16-15 Potential energy diagrams showing the effect of a catalyst. The catalyst provides a different mechanism, corresponding to a lower-energy pathway, for the formation of the products. A catalyzed reaction typically occurs in several steps, each with its own barrier, but the overall energy barrier for the net reaction, E'_a , is lower than that for the uncatalyzed reaction, E_a . The value of ΔE_{rxn} depends only on the states of the reactants and products (thermodynamics), so it is the same for either path.

Unless otherwise noted, all content on this page is © Cengage Learning.

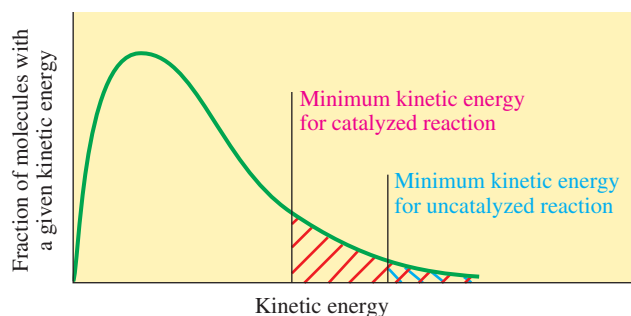
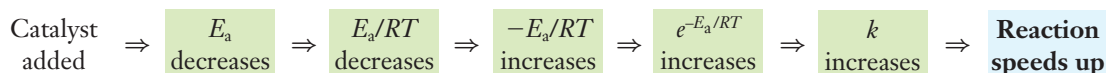


Figure 16-16 When a catalyst is present, the energy barrier is lowered. Thus, more molecules possess the minimum kinetic energy necessary for reaction. This is analogous to allowing more students to pass a course by lowering the requirements.

proceeds. The catalyst can then interact with more reactants to convert them into products. An effective catalyst can perform millions of such cycles. Because it is continually regenerated, a catalyst does not appear either as a reactant or as a product in the balanced equation for the reaction.

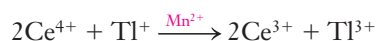
For constant T and the same concentrations,



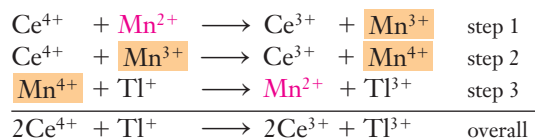
We can describe two categories of catalysts: (1) homogeneous catalysts and (2) heterogeneous catalysts.

Homogeneous Catalysis

A **homogeneous catalyst** exists in the same phase as the reactants. Ceric ion, Ce^{4+} , was at one time an important laboratory oxidizing agent used in many redox titrations (see Section 11.6). For example, Ce^{4+} oxidizes thallium(I) ions in solution; this reaction is catalyzed by the addition of a very small amount of a soluble salt containing manganese(II) ions, Mn^{2+} . The Mn^{2+} acts as a homogeneous catalyst.



This reaction is thought to proceed by the following sequence of elementary steps.

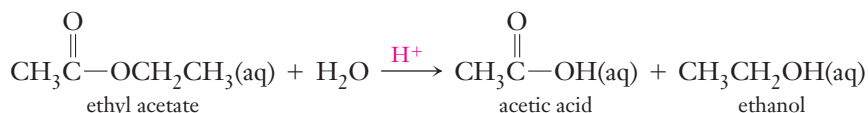


Some of the Mn^{2+} catalyst reacts in Step 1, but an equal amount is regenerated in Step 3 and is thus available to react again. The two ions shown on an orange background, Mn^{3+} and Mn^{4+} , are *reaction intermediates*. Mn^{3+} ions are formed in Step 1 and consumed in an equal amount in Step 2; similarly, Mn^{4+} ions are formed in Step 2 and consumed in an equal amount in Step 3.

We can now summarize the species that can appear in a reaction mechanism.

1. **Reactant:** More is consumed than is formed.
2. **Product:** More is formed than is consumed.
3. **Reaction intermediate:** Formed in earlier steps, then consumed in an equal amount in later steps.
4. **Catalyst:** Consumed in earlier steps, then regenerated in an equal amount in later steps.

Strong acids function as homogeneous catalysts in the acid-catalyzed hydrolysis of esters (a class of organic compounds—Section 23-14). Using ethyl acetate (a component of nail polish removers) as an example of an ester, we can write the overall reaction as follows.



This is a thermodynamically favored reaction, but because of its high energy of activation, it occurs only very, very slowly when no catalyst is present. In the presence of strong acids, however, the reaction occurs more rapidly. In this acid-catalyzed hydrolysis, different intermediates with lower activation energies are formed. The sequence of steps in the *proposed* mechanism is shown at the bottom of this page.

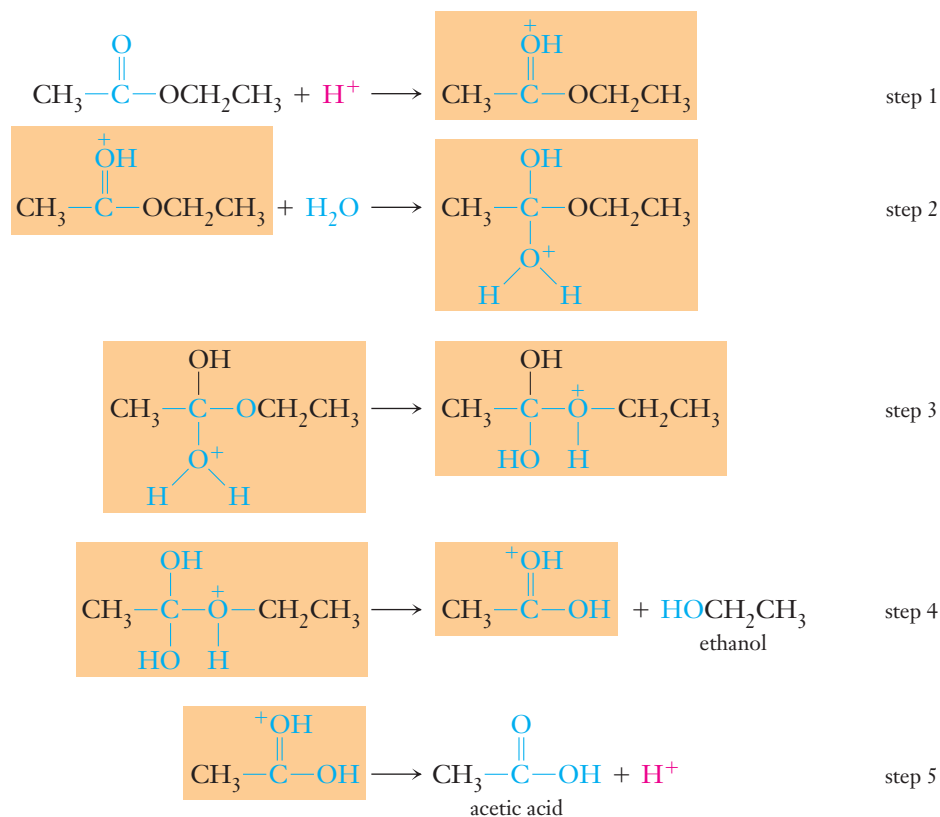
We see that H^+ is a reactant in Step 1, but it is completely regenerated in Step 5. H^+ is therefore a catalyst. The species shown on orange backgrounds in Steps 1 through 4 are *reaction intermediates*. Ethyl acetate and water are the reactants, and acetic acid and ethanol are the products of the overall catalyzed reaction.

► “Hydrolysis” means reaction with water.

► All intermediates in this sequence of elementary steps are charged species, but this is not always the case.

Heterogeneous Catalysis

A **heterogeneous catalyst** is present in a different phase from the reactants. Such catalysts are usually solids, and they lower activation energies by providing surfaces on which reactions can occur. The first step in the catalytic process is usually *adsorption*, in which one or more of the reactants become attached to the solid surface. Some reactant molecules



► Groups of atoms that are involved in the change in each step are shown in blue. The catalyst, H^+ , is shown in red. The intermediates are shown on an orange background.

Courtesy of Englehard Corporation



The petroleum industry uses numerous heterogeneous catalysts. Many of them contain highly colored compounds of transition metal ions. Several are shown here.

► Approximately 98% of all catalysts used in industry are heterogeneous. Therefore, when industrial chemists talk about a “catalyst,” they usually mean a heterogeneous catalyst.

► At the high temperatures of the combustion of any fuel in air, nitrogen and oxygen combine to form nitrogen oxide.

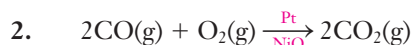
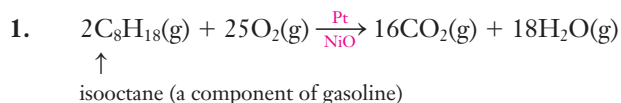
► See the Chemistry in Use essay “Nitrogen Oxides and Photochemical Smog” in Chapter 28.

► Maintaining the continued efficiency of all three reactions in a “three-way” catalytic converter is a delicate matter. It requires control of such factors as the O_2 supply pressure and the order in which the reactants reach the catalyst. Modern automobile engines use microcomputer chips, based on an O_2 sensor in the exhaust stream, to control air valves.

may be held in particular orientations, or some bonds may be weakened; in other molecules, some bonds may be broken to form atoms or smaller molecular fragments. This causes *activation* of the reactants. As a result, *reaction* occurs more readily than would otherwise be possible. In a final step, *desorption*, the product molecules leave the surface, freeing reaction sites to be used again. Most heterogeneous catalysts are more effective as small particles, because they have relatively large surface areas.

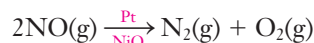
Transition metals and their compounds function as effective catalysts in many homogeneous and heterogeneous reactions. Vacant *d* orbitals in many transition metal ions can accept electrons from reactants to form intermediates. These subsequently decompose to form products. Three transition metals, Pt, Pd, and Ni, are often used as finely divided solids to provide surfaces on which heterogeneous reactions can occur.

The catalytic converters (Figure 16-17) built into automobile exhaust systems contain two types of heterogeneous catalysts, powdered noble metals and powdered transition metal oxides. They catalyze the oxidation of unburned hydrocarbon fuel (reaction 1) and of partial combustion products such as carbon monoxide (reaction 2, shown in Figure 16-18).



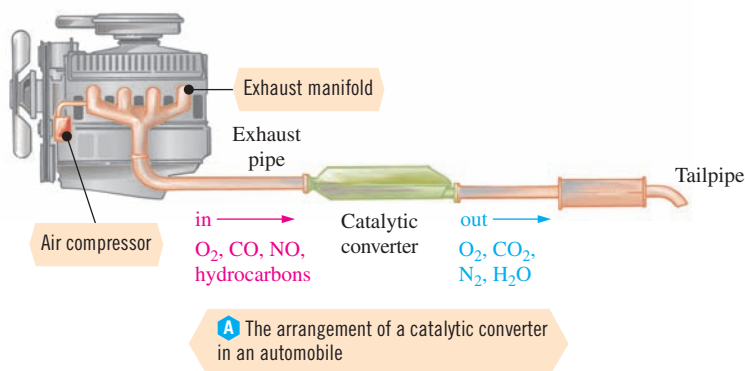
It is desirable to carry out these reactions in automobile exhaust systems. Carbon monoxide is very poisonous. The latter reaction is so slow that a mixture of CO and O_2 gas at the exhaust temperature would remain unreacted for thousands of years in the absence of a catalyst! Yet the addition of only a small amount of a solid, finely divided transition metal catalyst promotes the production of up to a mole of CO_2 per minute. Because this reaction is a very simple but important one, it has been studied extensively by surface chemists. It is one of the best understood heterogeneously catalyzed reactions. The major features of the catalytic process are shown in Figure 16-18.

The same catalysts also catalyze another reaction, the decomposition of nitrogen oxide, NO, into harmless N_2 and O_2 .



Nitrogen oxide is a serious air pollutant because it is oxidized to nitrogen dioxide, NO_2 , which reacts with water to form nitric acid, and with other products of the incomplete combustion of hydrocarbons to form nitrates. The latter are eye irritants in photochemical smog.

These three reactions, catalyzed in catalytic converters, are all exothermic and thermodynamically favored. Unfortunately, other energetically favored reactions are also accelerated by the mixed catalysts. All fossil fuels contain sulfur compounds, which are oxidized to sulfur dioxide during combustion. Sulfur dioxide, itself an air pollutant, undergoes further oxidation to form sulfur trioxide as it passes through the catalytic bed.



B A cutaway view of a catalytic converter, showing the pellets of catalyst

Figure 16-17 A catalytic converter.

Unless otherwise noted, all content on this page is © Cengage Learning.

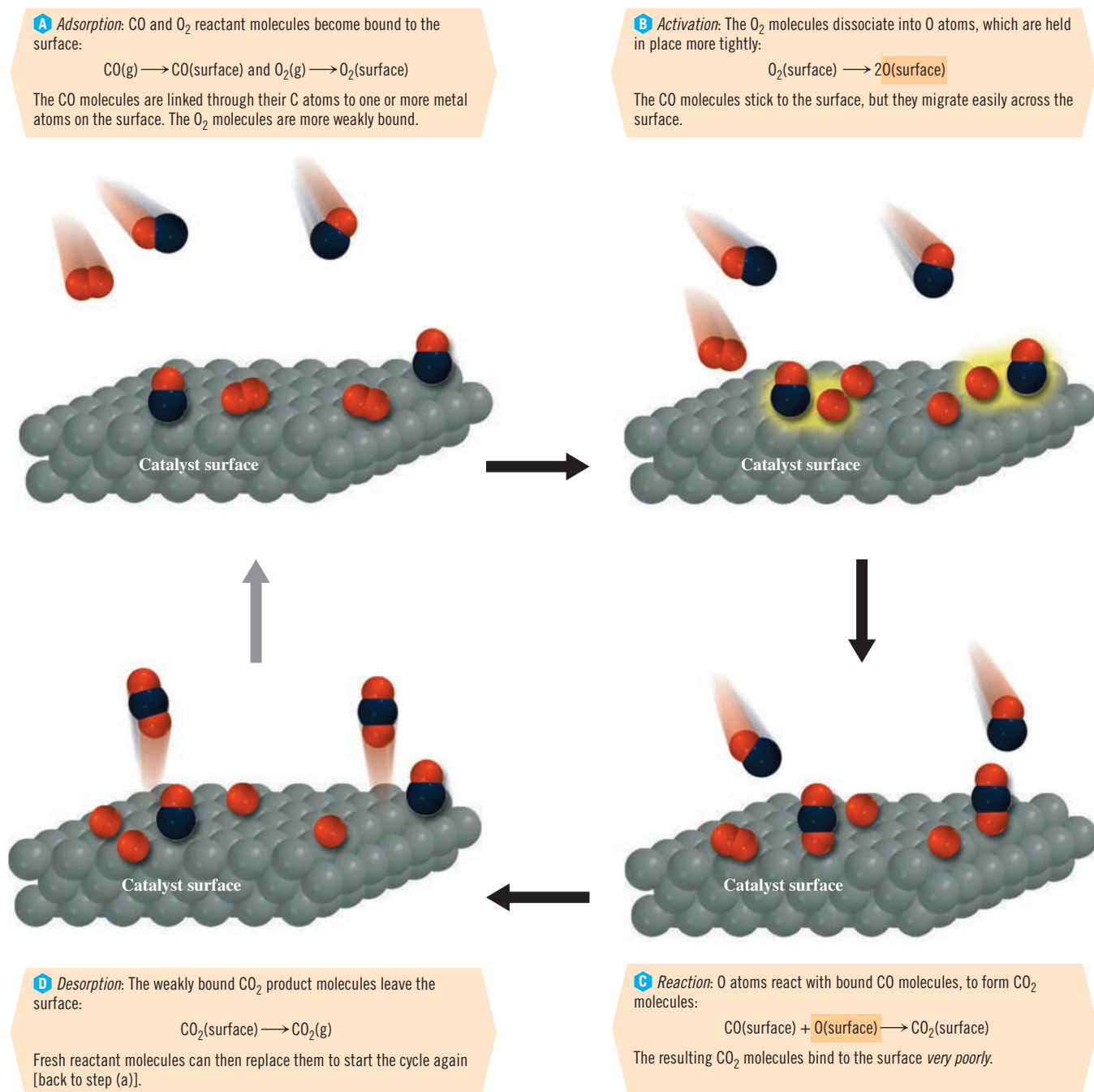
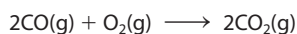
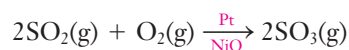


Figure 16-18 A schematic representation of the catalysis of the reaction



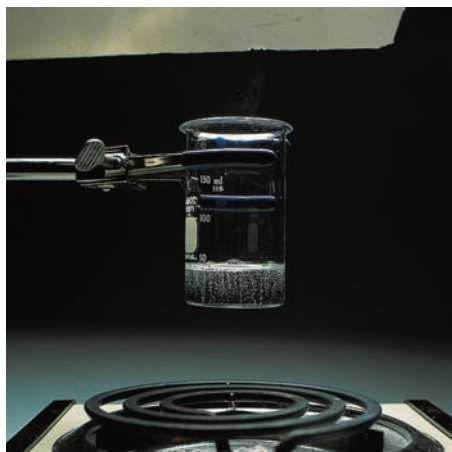
on a metallic surface.



Sulfur trioxide is probably a worse pollutant than sulfur dioxide, because SO₃ is the acid anhydride of strong, corrosive sulfuric acid. Sulfur trioxide reacts quickly with water vapor in the air, as well as in auto exhausts, to form sulfuric acid droplets. This problem must be overcome if the current type of catalytic converter is to see continued use. These same catalysts also suffer from the problem of being “poisoned”—that is, made inactive—by lead. Leaded fuels contain tetraethyl lead, Pb(C₂H₅)₄, and tetramethyl lead, Pb(CH₃)₄. Such fuels

Unless otherwise noted, all content on this page is © Cengage Learning.

Charles D. Winters



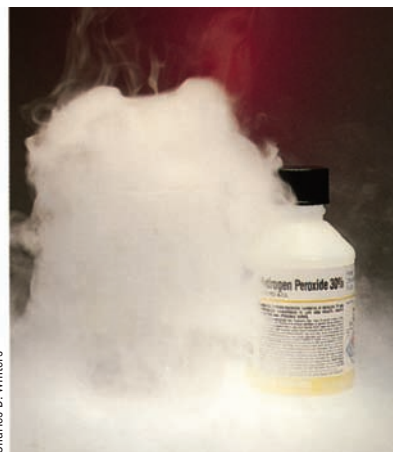
A This reaction takes place more rapidly if the solution is heated.

Charles D. Winters



B A very small amount of a transition metal oxide is added.

Charles D. Winters



C This oxide catalyzes the decomposition reaction. The catalyzed reaction is rapid, so the exothermic reaction quickly heats the solution to the boiling point of water, forming steam. The temperature increase further accelerates the decomposition. We should never use a syringe with a metal tip to withdraw a sample from a 30% hydrogen peroxide solution, because the metal can dangerously catalyze the rapid decomposition.

A 30% hydrogen peroxide, H_2O_2 , solution at room temperature decomposes very slowly to form O_2 and H_2O .



Charles D. Winters

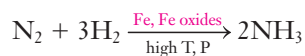
The bombardier beetle uses a catalyzed decomposition of hydrogen peroxide as a means of defense. An enzyme produced by the beetle catalyzes the rapid exothermic reaction. The resulting steam, along with other irritating chemical, is then ejected.

are not suitable for automobiles equipped with catalytic converters and are banned by U.S. law.

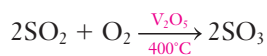
Reactions that occur in the presence of a solid catalyst, as on a metal surface (heterogeneous catalysis), often follow zero-order kinetics. For instance, the rate of decomposition of $\text{NO}_2(\text{g})$ at high pressures on a platinum metal surface does not change if we add more NO_2 . This is because only the NO_2 molecules on the surface can react. If the metal surface is completely covered with NO_2 molecules, no additional molecules can be *adsorbed* until the ones already there have reacted and the products have *desorbed*. Thus, the rate of the reaction is controlled only by the availability of reaction sites on the Pt surface, and not by the total number of NO_2 molecules available.

Some other important reactions that are catalyzed by transition metals and their oxides follow.

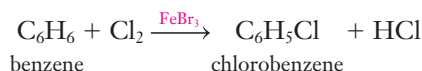
1. The Haber process for the production of ammonia (see Section 17-7).



2. The contact process for the production of sulfur trioxide in the manufacture of sulfuric acid (see Section 28-11).



3. The chlorination of benzene (see Section 23-16).



4. The hydrogenation of unsaturated hydrocarbons (see Section 23-17).



Enzymes as Biological Catalysts

Enzymes are proteins that act as catalysts for specific biochemical reactions in living systems. The reactants in enzyme-catalyzed reactions are called **substrates**. Thousands of vital processes in our bodies are catalyzed by many different enzymes. For instance, the enzyme carbonic anhydrase catalyzes the combination of CO_2 and water (the substrates), facilitating most of the transport of carbon dioxide in the blood. This combination reaction, ordinarily slow, proceeds rapidly in the presence of carbonic anhydrase; a single molecule of this enzyme can promote the conversion of more than 1 million molecules of carbon dioxide each second. Each enzyme is extremely specific, catalyzing only a few closely related reactions—or, in many cases, only one particular reaction—for only certain substrates. Modern theories of enzyme action attribute this to the requirement of very specific matching of shapes (molecular geometries) and polarities for a particular substrate to bind to a particular enzyme (Figure 16-19).

Enzyme-catalyzed reactions are important examples of zero-order reactions; that is, the rate of such a reaction is independent of the concentration of the substrate (provided some substrate is present).

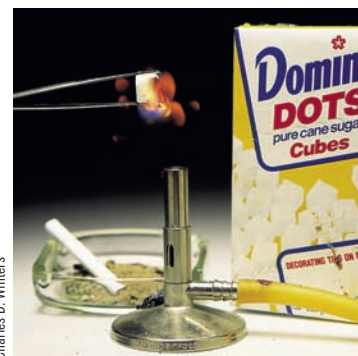
$$\text{rate} = k$$

Each active site on an enzyme molecule can bind to only one substrate molecule at a time (or one pair, if the reaction links two reactant molecules), no matter how many other substrate molecules are available in the vicinity.

Ammonia is a very important industrial chemical that is used as a fertilizer and in the manufacture of many other chemicals. The reaction of nitrogen with hydrogen is a thermodynamically spontaneous reaction (product-favored), but without a catalyst it is very slow, even at high temperatures. The Haber process for its preparation involves the use of iron as a catalyst at 450°C to 500°C and high pressures.

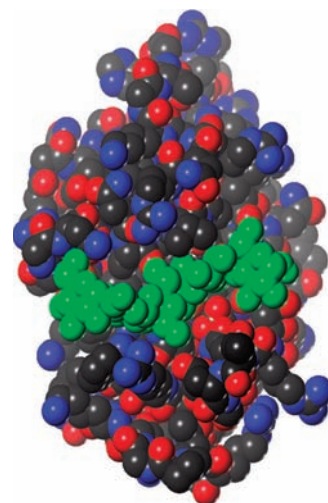


Even so, iron is not a very effective catalyst even under these extreme conditions.



Charles D. Winters

When heated, a sugar cube (sucrose, melting point 185°C) melts but does not burn. A sugar cube rubbed in cigarette ash burns before it melts. The cigarette ash contains trace amounts of metal compounds that catalyze the combustion of sugar.



George Stanley

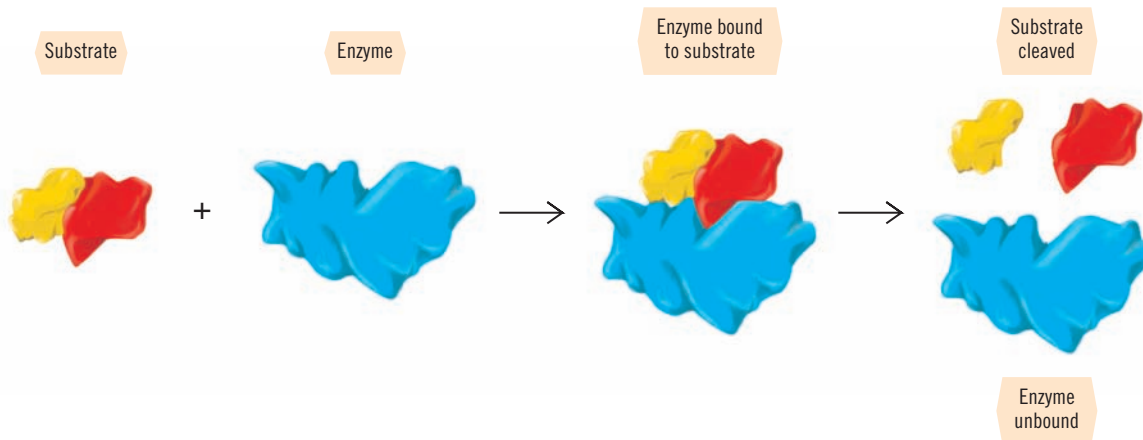


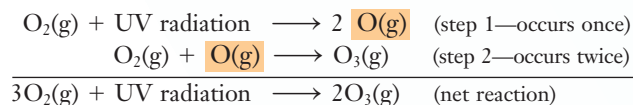
Figure 16-19 A schematic representation of a simplified mechanism (lock-and-key) for enzyme reaction. The substrates (reactants) fit the active sites of the enzyme molecule much as keys fit locks. When the reaction is complete, the products do not fit the active sites as well as the reactants did. They separate from the enzyme, leaving it free to catalyze the reaction of additional reactant molecules. The enzyme is not permanently changed by the process. The illustration here is for a process in which a complex reactant molecule is split to form two simpler product molecules. The formation of simple sugars from complex carbohydrates is a similar reaction. Some enzymes catalyze the combination of simple molecules to form more complex ones.

CHEMISTRY IN USE

Ozone

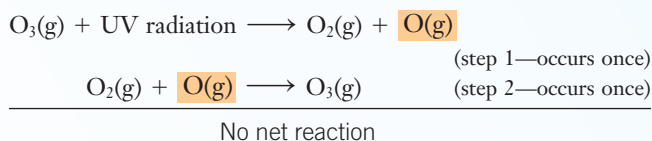
Ozone, O_3 , is such a powerful oxidizing agent that in significant concentrations it degrades many plastics, metals, and rubber, as well as both plant and animal tissues. We therefore try to minimize exposure to ozone in our immediate environment. In the upper atmosphere, however, ozone plays a very important role in the absorption of harmful radiation from the sun. Maintaining appropriate concentrations of ozone—minimizing its production where ozone is harmful and preventing its destruction where ozone is helpful—is an important challenge in environmental chemistry.

Ozone is formed in the upper atmosphere as some O_2 molecules absorb high-energy UV radiation from the sun and dissociate into oxygen atoms; these then combine with other O_2 molecules to form ozone.



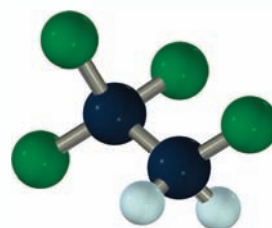
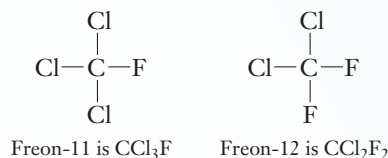
Although it also decomposes in the upper atmosphere, the ozone supply is continuously replenished by this process. Its concentration in the stratosphere ($\approx 7\text{--}31$ miles above the earth's surface) is about 10 ppm (parts per million), whereas it is only about 0.04 ppm near the earth's surface.

The high-altitude ozone layer is responsible for absorbing much of the dangerous ultraviolet light from the sun in the $20\text{--}30\text{ \AA}$ wavelength range.

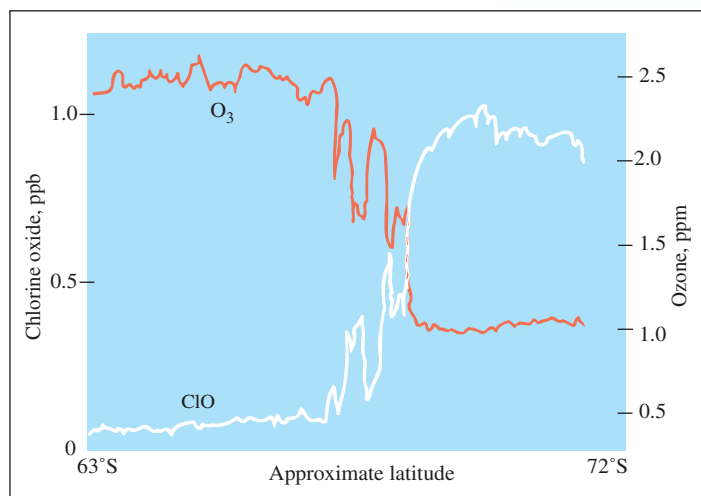


We see that each time this sequence takes place, it absorbs one photon of ultraviolet light; however, the process regenerates as much ozone as it uses up. Each stratospheric ozone molecule can thus absorb a significant amount of ultraviolet light. If this high-energy radiation reached the surface of the earth in higher intensity, it would be very harmful to plants and animals (including humans). It has been estimated that the incidence of skin cancer would increase by 2% for every 1% decrease in the concentration of ozone in the stratosphere.

Chlorofluorocarbons (CFCs) are chemically inert, nonflammable, nontoxic compounds that are superb solvents and have been used in many industrial processes; they are excellent coolants for air conditioners and refrigerators. Two CFCs that have been widely used are Freon-11 and Freon-12 (Freon is a DuPont trade name).



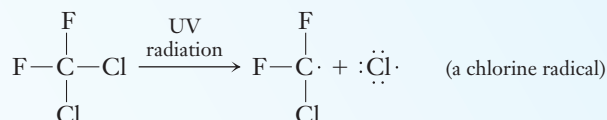
The compound known as HCFC-134, a fluorocarbon currently used in home and automobile air conditioners.



A plot that shows the decrease in $[O_3]$ as $[ClO]$ increases over Antarctica.

The CFCs are so unreactive that they do not readily decompose, that is, break down into simpler compounds, when they are released into the atmosphere. Over time the CFCs are carried into the stratosphere by air currents, where they are exposed to large amounts of ultraviolet radiation.

In 1974, Mario Molina and Sherwood Rowland of the University of California–Irvine demonstrated in their laboratory that when CFCs are exposed to high-energy ultraviolet radiation they break down to form chlorine *radicals*.

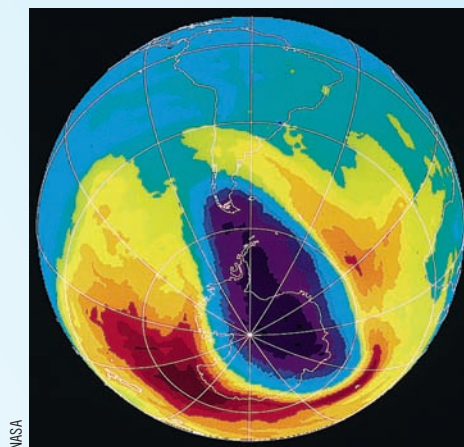
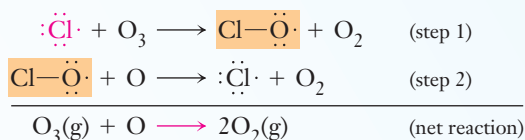


Molina and Rowland predicted that these very reactive radicals could cause problems by catalyzing the destruction of ozone in the stratosphere.

Each spring since 1979, researchers have observed a thinning of the ozone layer over Antarctica. Each spring (autumn in the Northern Hemisphere) beginning in 1983, satellite images have shown a “hole” in the ozone layer over the South Pole. During August and September 1987, a NASA research team flew a plane equipped with sophisticated analytical instruments into the ozone hole 25 times. Their measurements demonstrated that as the concentration of the chlorine oxide radicals, $\text{Cl}-\text{O}$, increased, the concentration of ozone decreased.

By September 1992, this *ozone hole* was nearly three times the area of the United States. In December 1994, three years of data from NASA’s Upper Atmosphere Research Satellite (UARS) provided conclusive evidence that CFCs are primarily responsible for this destruction of the ozone layer. Considerable thinning of the ozone layer in the Northern Hemisphere has also been observed.

The following is a simplified representation of the *chain reaction* that is now believed to account for most of the ozone destruction in the stratosphere.



A computer-generated image of part of the Southern Hemisphere on October 17, 1994, reveals the ozone “hole” (black and purple areas) over Antarctica and the tip of South America. Relatively low ozone levels (blue and green areas) extend into much of South America as well as Central America. Normal ozone levels are shown in yellow, orange, and red. The ozone hole is not stationary but moves about as a result of air currents.

A sufficient supply of oxygen atoms, O , is available in the upper atmosphere for the second step to occur. The net reaction results in the destruction of a molecule of ozone. The chlorine radical that initiates the first step of this reaction sequence is regenerated in the second step, however, and so a single chlorine radical can act as a catalyst to destroy many thousands of O_3 molecules. Other well-known reactions also destroy ozone in the stratosphere, but the evidence shows conclusively that CFCs are the principal culprits.

Since January 1978, the use of CFCs in aerosol cans in the United States has been banned; increasingly strict laws prohibit the release into the atmosphere of CFCs from sources such as automobile air conditioners and discarded refrigerators. The Montreal Protocol, signed by 24 countries in 1989, called for reductions in production and use of many CFCs. International agreements have since called for a complete ban on CFC production. Efforts to develop suitable replacement substances and controls for existing CFCs continue. The good news is that scientists expect the ozone hole to decrease and possibly disappear during the 21st century *if* current international treaties remain in effect and *if* they are implemented throughout the world. These are two very large *ifs*.

Up to date information on stratospheric ozone can be found at the NASA website, ozonewatch.gsfc.nasa.gov/ and at other websites.

► The process is called nitrogen fixation. The ammonia can be used in the synthesis of many nitrogen-containing biological compounds such as proteins and nucleic acids.

► Transition metal ions are present in the active sites of some enzymes.

In contrast, the reaction between N_2 and H_2 to form NH_3 is catalyzed at room temperature and atmospheric pressure by a class of enzymes, called nitrogenases, that are present in some bacteria. Legumes are plants that support these bacteria; they are able to obtain nitrogen as N_2 from the atmosphere and convert it to ammonia.

In comparison with manufactured catalysts, most enzymes are tremendously efficient under very mild conditions. If chemists and biochemists could develop catalysts with a small fraction of the efficiency of enzymes, such catalysts could be a great boon to the world's health and economy. One of the most active areas of current chemical research involves attempts to discover or synthesize catalysts that can mimic the efficiency of naturally occurring enzymes such as nitrogenases. Such a development would be important in industry. Due to the high temperatures and pressures needed, an estimated 1% of the world's energy supply is used each year to run the Haber process. Developing better catalysts could decrease the cost of food grown with the aid of ammonia-based fertilizers. Ultimately this would help greatly to feed the world's growing population.

KEY TERMS

Activation energy The kinetic energy that reactant molecules must have to allow them to reach the transition state so that a reaction can occur; also known as the *activation barrier*.

Arrhenius equation An equation that relates the specific rate constant to activation energy and temperature.

Catalyst A substance that increases the rate at which a reaction occurs. It is regenerated during the course of the reaction and can then interact with more reactants to convert them into products.

Chemical kinetics The study of rates and mechanisms of chemical reactions and of the factors on which they depend.

Collision theory A theory of reaction rates that states that effective collisions between reactant molecules must take place for reaction to occur.

Effective collision A collision between molecules that results in reaction; one in which molecules collide with proper orientations and with sufficient energy to react.

Elementary step An individual step in the mechanism by which a reaction occurs. For each elementary step, the reaction orders *do* match the reactant coefficients in that step.

Enzyme A protein that acts as a catalyst in a biological system.

Fundamental step See *Elementary step*.

Half-life of a reactant ($t_{1/2}$) The time required for half of that reactant to be converted into product(s).

Heterogeneous catalyst A catalyst that exists in a different phase (solid, liquid, or gas) from the reactants; the vast majority of heterogeneous catalysts are solids.

Homogeneous catalyst A catalyst that exists in the same phase (liquid or gas) as the reactants.

Integrated rate equation An equation that relates the concentration of a reactant remaining to the time elapsed; has different mathematical forms for different orders of reaction.

Method of initial rates A method of determining the rate-law expression by carrying out a reaction with different initial concentrations and analyzing the resulting changes in initial rates.

Order of a reactant The power to which the reactant's concentration is raised in the rate-law expression.

Order of a reaction The sum of the powers to which all concentrations are raised in the rate-law expression; also called the overall order of a reaction.

Rate constant An experimentally determined proportionality constant that is different for different reactions and that, for a given reaction, changes only with temperature or the presence of a catalyst; k in the rate-law expression, $\text{rate} = k[\text{A}]^x[\text{B}]^y$; also known as the *specific rate constant*.

Rate-determining step The slowest elementary step in a reaction mechanism; the step that limits the overall rate of reaction.

Rate-law expression An equation that relates the rate of a reaction to the concentrations of the reactants and the specific rate constant; $\text{rate} = k[\text{A}]^x[\text{B}]^y$. The exponents of reactant concentrations *do not necessarily* match the coefficients in the overall balanced chemical equation. The rate-law expression must be determined from experimental data; also known as the *rate law*.

Rate of reaction The change in concentration of a reactant or product per unit time.

Reaction coordinate The progress along the potential energy pathway from reactants to products.

Reaction intermediate A species that is produced and then entirely consumed during a multistep reaction; usually short-lived.

Reaction mechanism The sequence of fundamental steps by which reactants are converted into products.

Substrate A reactant in an enzyme-catalyzed reaction.

Thermodynamically favorable (spontaneous) reaction A reaction that occurs with a net release of free energy, G ; a reaction for which ΔG is negative (see Section 15-16).

Transition state A relatively high-energy state in which bonds in reactant molecules are partially broken and new ones are partially formed.

Transition state theory A theory of reaction rates that states that reactants pass through high-energy transition states before forming products.

EXERCISES

● Molecular Reasoning exercises

▲ More Challenging exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

General Concepts

- Briefly summarize the effects of each of the four factors that affect rates of reactions.
- Describe the basic features of collision theory and transition state theory.
- What is a rate-law expression? Describe how it is determined for a particular reaction.
- Distinguish between reactions that are thermodynamically favorable and reactions that are kinetically favorable. What can be said about the relationship between the two?
- What is meant by the mechanism of a reaction? How does the mechanism relate to the order of the reaction?
- What, if anything, can be said about the relationship between the coefficients of the balanced *overall* equation for a reaction and the powers to which concentrations are raised in the rate-law expression? To what are these powers related?
- Express the rate of the reaction
 $2\text{N}_2\text{H}_4(\ell) + \text{N}_2\text{O}_4(\ell) \longrightarrow 3\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$
 in terms of: (a) $\Delta[\text{N}_2\text{O}_4]$; (b) $\Delta[\text{N}_2]$.
- Express the rate of reaction in terms of the rate of change of each reactant and each product in the following equations.
 (a) $3\text{ClO}^-(\text{aq}) \longrightarrow \text{ClO}_3^-(\text{aq}) + 2\text{Cl}^-(\text{aq})$
 (b) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{SO}_3(\text{g})$
 (c) $\text{C}_2\text{H}_4(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_4\text{Br}_2(\text{g})$
 (d) $(\text{C}_2\text{H}_5)_2(\text{NH})_2 + \text{I}_2 \longrightarrow (\text{C}_2\text{H}_5)_2\text{N}_2 + 2\text{HI}$
 (liquid phase)
- At a given time, N_2 is reacting with H_2 at a rate of 0.30 M/min to produce NH_3 . At that same time, what is the rate at which the other reactant is changing and the rate at which the product is changing?

$$\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$$
- The following equation shows the production of NO and H_2O by oxidation of ammonia. At a given time, NH_3 is reacting at a rate of 1.20 M/min . At that same time, what is the rate at which the other reactant is changing and the rate at which each product is changing?

$$4\text{NH}_3 + 5\text{O}_2 \longrightarrow 4\text{NO} + 6\text{H}_2\text{O}$$
- Why do large crystals of sugar burn more slowly than finely ground sugar?
- Some fireworks are bright because of the burning of magnesium. Speculate on how fireworks might be constructed using magnesium. How might the sizes of the pieces of magnesium be important? What would

you expect to occur if the pieces that were used were too large? too small?



Rate-Law Expression

- A reaction has the experimental rate equation: $\text{Rate} = k[\text{A}]^2$. How will the rate change if the concentration of A is tripled? If the concentration of A is halved?
- The rate expression for the following reaction at a certain temperature is $\text{rate} = k[\text{NO}]^2[\text{O}_2]$. Two experiments involving this reaction are carried out at the same temperature. In the second experiment the initial concentration of NO is halved, while the initial concentration of O_2 is doubled. The initial rate in the second experiment will be how many times that of the first?

$$2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$$
- The rate-law expression for the following reaction is found to be $\text{rate} = k[\text{N}_2\text{O}_5]$. What is the overall reaction order?

$$2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$$
- Use times expressed in seconds to give the units of the rate constant for reactions that are overall (a) first order; (b) second order; (c) third order; (d) of order $1\frac{1}{2}$.
- Rate data were obtained at 25°C for the following reaction. What is the rate-law expression for this reaction?

$$\text{A} + 2\text{B} \longrightarrow \text{C} + 2\text{D}$$

Expt.	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial Rate of Formation of C ($\text{M} \cdot \text{min}^{-1}$)
1	0.10	0.10	3.0×10^{-4}
2	0.30	0.30	9.0×10^{-4}
3	0.10	0.30	3.0×10^{-4}
4	0.20	0.40	6.0×10^{-4}

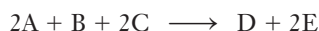
● Molecular Reasoning exercises

▲ More Challenging exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

18. Rate data were obtained for the following reaction at 25°C. What is the rate-law expression for the reaction?



Expt.	Initial [A] (M)	Initial [B] (M)	Initial [C] (M)	Initial Rate of Formation of D (M · min ⁻¹)
1	0.10	0.10	0.20	5.0×10^{-4}
2	0.20	0.30	0.20	1.5×10^{-3}
3	0.30	0.10	0.20	5.0×10^{-4}
4	0.40	0.30	0.60	4.5×10^{-3}

19. The reaction of CO(g) + NO₂(g) is second-order in NO₂ and zeroth-order in CO at temperatures less than 500 K.
 (a) Write the rate law for the reaction.
 (b) How will the reaction rate change if the NO₂ concentration is halved?
 (c) How will the reaction rate change if the concentration of CO is doubled?
20. Listed below are the equations for three reactions and the rate-law expressions for them.

Reaction	Rate Law
$2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	$\text{rate} = k[\text{NO}]^2 [\text{H}_2]$
$2\text{ICl}(\text{g}) + \text{H}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g}) + \text{I}_2(\text{g})$	$\text{rate} = k[\text{ICl}] [\text{H}_2]$
$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow 2\text{HBr}(\text{g})$	$\text{rate} = k[\text{H}_2] [\text{Br}_2]$

For which of these reactions will doubling the concentration of H₂ double the reaction rate? For which of these reactions will doubling the concentration of H₂ quadruple the reaction rate? For which of these reactions will doubling the concentration of H₂ have no effect on the rate of the reaction?

21. For a reaction involving the decomposition of Y, the following data are obtained:

Rate (mol/L · min)	0.228	0.245	0.202	0.158
[Y]	0.200	0.170	0.140	0.110

- (a) Determine the order of the reaction.
 (b) Write the rate expression for the decomposition of Y.
 (c) Calculate k for the above experiment.
22. Rate data were collected for the following reaction at a particular temperature.
- $$2\text{ClO}_2(\text{aq}) + 2\text{OH}^-(\text{aq}) \longrightarrow \text{ClO}_3^-(\text{aq}) + \text{ClO}_2^-(\text{aq}) + \text{H}_2\text{O}(\ell)$$
- | Expt. | Initial [ClO ₂] (mol/L) | Initial [OH ⁻] (mol/L) | Initial Rate of Formation of ClO ₃ ⁻ (M s ⁻¹) |
|-------|-------------------------------------|------------------------------------|---|
| 1 | 0.012 | 0.012 | 2.07×10^{-4} |
| 2 | 0.012 | 0.024 | 4.14×10^{-4} |
| 3 | 0.024 | 0.012 | 8.28×10^{-4} |
| 4 | 0.024 | 0.024 | 1.66×10^{-3} |

- (a) What is the rate-law expression for this reaction?
 (b) Describe the order of the reaction with respect to each reactant and to the overall order. (c) What is the value, with units, for the specific rate constant?

23. The reaction



gives the following initial rates.

Expt.	[(C ₂ H ₅) ₂ (NH) ₂] ₀ (mol/L)	[I ₂] ₀ (mol/L)	Initial Rate of Formation of (C ₂ H ₅) ₂ N ₂ (M · s ⁻¹)
1	0.015	0.015	$3.15 \text{ M} \cdot \text{s}^{-1}$
2	0.015	0.045	$9.45 \text{ M} \cdot \text{s}^{-1}$
3	0.030	0.045	$18.9 \text{ M} \cdot \text{s}^{-1}$

- (a) Write the rate-law expression. (b) What is the value, with units, for the specific rate constant?

24. ▲ Given these data for the reaction A + B → C, write the rate-law expression.

Expt.	Initial [A] (M)	Initial [B] (M)	Initial Rate of Formation of C (M · s ⁻¹)
1	0.10	0.20	5.0×10^{-6}
2	0.10	0.30	7.5×10^{-6}
3	0.20	0.40	4.0×10^{-5}

25. ▲ (a) Given these data for the reaction A + B → C, write the rate-law expression. (b) What is the value, with units, for the specific rate constant?

Expt.	Initial [A] (M)	Initial [B] (M)	Initial Rate of Formation of C (M · s ⁻¹)
1	0.25	0.15	8.0×10^{-5}
2	0.25	0.30	3.2×10^{-4}
3	0.50	0.60	5.12×10^{-3}

26. ▲ (a) Given these data for the reaction A + B → C, write the rate-law expression. (b) What is the value, with units, for the specific rate constant?

Expt.	Initial [A] (M)	Initial [B] (M)	Initial Rate of Formation of C (M/s)
1	0.10	0.10	2.0×10^{-4}
2	0.10	0.20	8.0×10^{-4}
3	0.20	0.40	2.56×10^{-2}

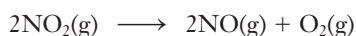
27. ▲ Consider a chemical reaction between compounds A and B that is first order in A and first order in B. From the information shown here, fill in the blanks.

Expt.	Rate ($M \cdot s^{-1}$)	[A]	[B]
1	0.24	0.20 M	0.050 M
2	0.20	_____ M	0.030 M
3	0.80	0.40 M	_____ M

28. ▲ Consider a chemical reaction of compounds A and B that was found to be first order in A and second order in B. From the following information, fill in the blanks.

Expt.	Rate ($M \cdot s^{-1}$)	[A]	[B]
1	0.150	1.00 M	0.200 M
2	_____	2.00 M	0.200 M
3	_____	2.00 M	0.400 M

29. ▲ The rate of decomposition of NO_2 by the following reaction at a particular temperature is $5.4 \times 10^{-5} \text{ mol NO}_2/\text{L} \cdot \text{s}$ when $[\text{NO}_2] = 0.0110 \text{ mol/L}$.



- (a) Assume that the rate law is $\text{rate} = k[\text{NO}_2]$. What rate of disappearance of NO_2 would be predicted when $[\text{NO}_2] = 0.00550 \text{ mol/L}$? (b) Now assume that the rate law is $\text{rate} = k[\text{NO}_2]^2$. What rate of disappearance of NO_2 would be predicted when $[\text{NO}_2] = 0.00550 \text{ mol/L}$? (c) The rate when $[\text{NO}_2] = 0.00550 \text{ mol/L}$ is observed to be $1.4 \times 10^{-5} \text{ mol NO}_2/\text{L} \cdot \text{s}$. Which rate law is correct? (d) Calculate the rate constant. (Reminder: Express the rate of reaction in terms of rate of disappearance of NO_2 .)

Integrated Rate Equations and Half-Life

30. What is meant by the half-life of a reactant?
31. The rate law for the reaction of sucrose in water

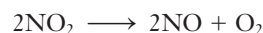


is $\text{rate} = k[\text{C}_{12}\text{H}_{22}\text{O}_{11}]$. After 2.57 hours at 25°C , 6.00 g/L of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ has decreased to 5.40 g/L. Evaluate k for this reaction at 25°C .



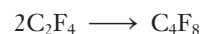
Sucrose (table sugar)

32. The rate constant for the decomposition of nitrogen dioxide



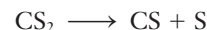
with a laser beam is $1.70 \text{ M}^{-1} \cdot \text{min}^{-1}$. Find the time, in seconds, needed to decrease 2.00 mol/L of NO_2 to 1.25 mol/L.

33. The second-order rate constant for the following gas-phase reaction is $0.0442 \text{ M}^{-1} \cdot \text{s}^{-1}$. We start with 0.135 mol C_2F_4 in a 2.00-liter container, with no C_4F_8 initially present.



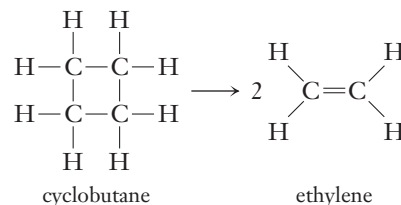
- (a) What will be the concentration of C_2F_4 after 1.00 hour? (b) What will be the concentration of C_4F_8 after 1.00 hour? (c) What is the half-life of the reaction for the initial C_2F_4 concentration given in part (a)? (d) How long will it take for half of the C_2F_4 that remains after 1.00 hour to disappear?

34. The decomposition reaction of carbon disulfide, CS_2 , to carbon monosulfide, CS , and sulfur is first order with $k = 2.8 \times 10^{-7} \text{ s}^{-1}$ at 1000°C .

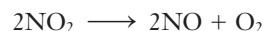


- (a) What is the half-life of this reaction at 1000°C ? (b) How many days would pass before a 2.00-gram sample of CS_2 had decomposed to the extent that 0.75 gram of CS_2 remained? (c) Refer to part (b). How many grams of CS would be present after this length of time? (d) How much of a 2.00-gram sample of CS_2 would remain after 45.0 days?

35. ▲ The first-order rate constant for the conversion of cyclobutane to ethylene at 1000°C is 87 s^{-1} . (a) What is the half-life of this reaction at 1000°C ? (b) If you started with 4.00 g of cyclobutane, how long would it take to consume 2.50 g of it? (Hint: Write the ratio of concentrations, $[\text{A}]_0/[\text{A}]$, in terms of mass, molecular weight, and volume.) (c) How much of an initial 1.00-g sample of cyclobutane would remain after 1.00 s?



36. ▲ For the reaction



the rate equation is

$$\text{rate} = 1.4 \times 10^{-10} \text{ M}^{-1} \cdot \text{s}^{-1} [\text{NO}_2]^2 \text{ at } 25^\circ\text{C}$$

- (a) If 3.00 mol of NO_2 is initially present in a sealed 2.00-L vessel at 25°C , what is the half-life of the reaction? (b) Refer to part (a). What concentration and how many grams of NO_2 remain after 115 years? (c) Refer to part (b). What concentration of NO would have been produced during the same period of time?



Molecular Reasoning exercises



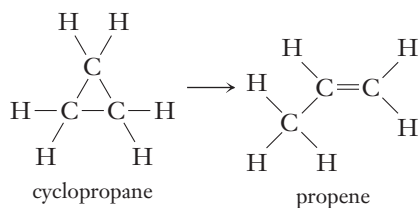
More Challenging exercises

Blue-Numbered exercises

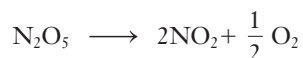
exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

37. The first-order rate constant for the radioactive decay of radium-223 is 0.0606 day^{-1} . What is the half-life of radium-223?
38. Cyclopropane rearranges to form propene in a reaction that follows first-order kinetics. At 800. K, the specific rate constant for this reaction is $2.74 \times 10^{-3} \text{ s}^{-1}$. Suppose we start with a cyclopropane concentration of 0.290 M . How long will it take for 99.0% of the cyclopropane to disappear according to this reaction?



39. The rate constant for the first-order reaction



- is $1.20 \times 10^{-2} \text{ s}^{-1}$ at 45°C , and the initial concentration of N_2O_5 is 0.01500 M . (a) How long will it take for the concentration to decrease to 0.00100 M ? (b) How much longer will it take for a further decrease to 0.000900 M ?
40. The familiar rule of thumb that the rate of a reaction roughly doubles for every 10°C rise in temperature (around room temperature) has been shown to be consistent with the Arrhenius equation, using a typical activation energy of 50 kJ/mol . How much would the rate of such a reaction change if the temperature of the reaction were changed from 90°C to 100°C or from 0°C to 10°C ?
41. The thermal decomposition of ammonia at high temperatures was studied in the presence of inert gases. Data at $2000. \text{ K}$ are given for a single experiment.

$$\text{NH}_3 \longrightarrow \text{NH}_2 + \text{H}$$

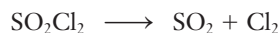
$t \text{ (hours)}$	$[\text{NH}_3] \text{ (mol/L)}$
0	8.000×10^{-7}
25	6.75×10^{-7}
50	5.84×10^{-7}
75	5.15×10^{-7}

Plot the appropriate concentration expressions against time to find the order of the reaction. Find the rate constant of the reaction from the slope of the line. Use the given data and the appropriate integrated rate equation to check your answer.

42. The following data were obtained from a study of the decomposition of a sample of HI on the surface of a gold wire. (a) Plot the data to find the order of the reaction, the rate constant, and the rate equation. (b) Calculate the HI concentration in mmol/L at $600. \text{ s}$.

$t \text{ (seconds)}$	$[\text{HI}] \text{ (mmol/L)}$
0.	5.46
250.	4.10
500.	2.73
750.	1.37

43. The decomposition of SO_2Cl_2 in the gas phase,



can be studied by measuring the concentration of Cl_2 as the reaction proceeds. We begin with $[\text{SO}_2\text{Cl}_2]_0 = 0.250 \text{ M}$. Holding the temperature constant at $320.^\circ\text{C}$, we monitor the Cl_2 concentration, with the following results.

$t \text{ (hours)}$	$[\text{Cl}_2] \text{ (mol/L)}$
0.00	0.000
2.00	0.037
4.00	0.068
6.00	0.095
8.00	0.117
10.00	0.137
12.00	0.153
14.00	0.168
16.00	0.180
18.00	0.190
20.00	0.199

- (a) Plot $[\text{Cl}_2]$ versus t . (b) Plot $[\text{SO}_2\text{Cl}_2]$ versus t . (c) Determine the rate law for this reaction. (d) What is the value, with units, for the specific rate constant at $320.^\circ\text{C}$? (e) How long would it take for 95% of the original SO_2Cl_2 to react?
44. ▲ At some temperature, the rate constant for the decomposition of HI on a gold surface is $0.080 \text{ M} \cdot \text{s}^{-1}$.
- $$2\text{HI(g)} \longrightarrow \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$$
- (a) What is the order of the reaction? (b) How long will it take for the concentration of HI to drop from 1.50 M to 0.15 M ?
45. At body temperature, the first-order rate constant is $1.87 \times 10^{-3} \text{ min}^{-1}$ for the elimination of the cancer chemotherapy agent cisplatin. What would be the concentration of cisplatin in a patient 36 hours after the concentration had reached $4.75 \times 10^{-3} \text{ M}$?
46. The first-order rate constant for the decomposition of an insecticide in moist soil is $3.0 \times 10^{-3} \text{ d}^{-1}$. How long will it take for 75% of the insecticide to decompose?

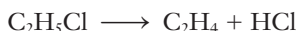
Activation Energy, Temperature, and Catalysts

47. The following rearrangement reaction is first order:



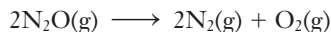
In a table of kinetics data, we find the following values listed for this reaction: $A = 3.98 \times 10^{13} \text{ s}^{-1}$, $E_a = 160. \text{ kJ/mol}$. (a) Calculate the value of the specific rate constant at room temperature, 25°C . (b) Calculate the value of the specific rate constant at 115°C .

48. The following gas-phase decomposition reaction is first order:



In a table of kinetics data, we find the following values listed for this reaction: $A = 1.58 \times 10^{13} \text{ s}^{-1}$, $E_a = 237 \text{ kJ/mol}$. (a) Calculate the value of the specific rate constant at room temperature, 25°C . (b) Calculate the value of the specific rate constant at 275°C .

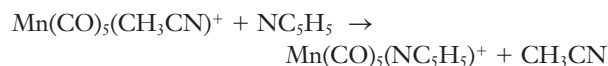
49. Draw typical reaction energy diagrams for one-step reactions that release energy and that absorb energy. Distinguish between the net energy change, ΔE , and the activation energy for each kind of reaction. Indicate potential energies of products and reactants for both kinds of reactions.
50. Use graphs to illustrate how the presence of a catalyst can affect the rate of a reaction.
51. How do homogeneous catalysts and heterogeneous catalysts differ?
52. (a) Why should one expect an increase in temperature to increase the initial rate of reaction? (b) Why should one expect a reaction in the gaseous state to be faster than the same reaction in the solid state?
53. Assume that the activation energy for a certain reaction is 173 kJ/mol and the reaction is started with equal initial concentrations of reactants. How many times faster will the reaction occur at 40°C than at 10°C ?
54. What is the activation energy for a reaction if its rate constant is found to triple when the temperature is raised from $600. \text{ K}$ to $610. \text{ K}$?
55. For a gas-phase reaction, $E_a = 103 \text{ kJ/mol}$, and the rate constant is 0.0850 min^{-1} at 273 K . Find the rate constant at 323 K .
56. The rate constant of a reaction is tripled when the temperature is increased from 298 K to 308 K . Find E_a .
57. The rate constant for the decomposition of N_2O



is $2.6 \times 10^{-11} \text{ s}^{-1}$ at $300.^\circ\text{C}$ and $2.1 \times 10^{-10} \text{ s}^{-1}$ at $330.^\circ\text{C}$. Calculate the activation energy for this reaction. Prepare a reaction coordinate diagram like Figure 16-10 using -164.1 kJ/mol as the ΔE_{rxn} .

58. For a particular reaction, $\Delta E = 51.51 \text{ kJ/mol}$, $k = 8.0 \times 10^{-7} \text{ s}^{-1}$ at 0.0°C , and $k = 8.9 \times 10^{-4} \text{ s}^{-1}$ at 50.0°C . Prepare a reaction coordinate diagram like Figure 16-10 for this reaction.

59. You are given the rate constant as a function of temperature for the exchange reaction



$T \text{ (K)}$	$k \text{ (min}^{-1}\text{)}$
298	0.0409
305	0.0818
312	0.157

(a) Calculate E_a from a plot of $\log k$ versus $1/T$. (b) Use the graph to predict the value of k at 308 K . (c) What is the numerical value of the collision frequency factor, A , in the Arrhenius equation?

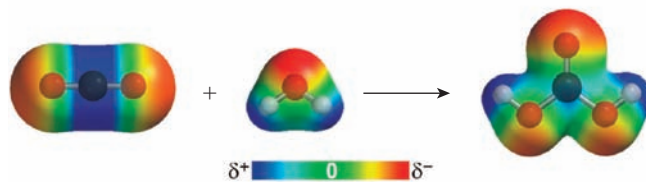
60. The rearrangement of cyclopropane to propene described in Exercise 38 has been studied at various temperatures. The following values for the specific rate constant have been determined experimentally.

$T \text{ (K)}$	$k \text{ (s}^{-1}\text{)}$
600.	3.30×10^{-9}
650.	2.19×10^{-7}
700.	7.96×10^{-6}
750.	1.80×10^{-4}
800.	2.74×10^{-3}
850.	3.04×10^{-2}
900.	2.58×10^{-1}

(a) From the appropriate plot of these data, determine the value of the activation energy for this reaction. (b) Use the graph to estimate the value of k at 500 K . (c) Use the graph to estimate the temperature at which the value of k would be equal to $5.00 \times 10^{-5} \text{ s}^{-1}$.

61. Biological reactions nearly always occur in the presence of enzymes as catalysts. The enzyme catalase, which acts on peroxides, reduces the E_a for the reaction from 72 kJ/mol (uncatalyzed) to 28 kJ/mol (catalyzed). By what factor does the reaction rate increase at normal body temperature, 37.0°C , for the same reactant (peroxide) concentration? Assume that the collision factor, A , remains constant.

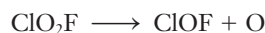
62. The enzyme carbonic anhydrase catalyzes the hydration of carbon dioxide.



This reaction is involved in the transfer of CO_2 from tissues to the lungs via the bloodstream. One enzyme molecule hydrates 10^6 molecules of CO_2 per second. How many grams of CO_2 are hydrated in one minute in 1 L by $1.0 \times 10^{-6} \text{ M}$ enzyme?

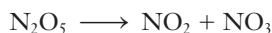


63. The following gas-phase reaction follows first-order kinetics.



The activation energy of this reaction is 186 kJ/mol. The value of k at 322°C is $6.76 \times 10^{-4} \text{ s}^{-1}$. (a) What would be the value of k for this reaction at 25°C? (b) At what temperature would this reaction have a k value of $3.00 \times 10^{-2} \text{ s}^{-1}$?

64. The following gas-phase reaction is first order.

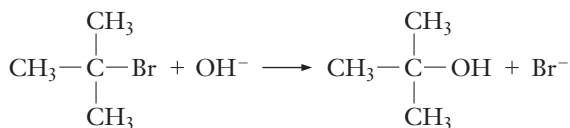


The activation energy of this reaction is 88 kJ/mol. The value of k at 0°C is $9.16 \times 10^{-3} \text{ s}^{-1}$. (a) What would be the value of k for this reaction at room temperature, 25°C? (b) At what temperature would this reaction have a k value of $3.00 \times 10^{-2} \text{ s}^{-1}$?

Reaction Mechanisms

65. Define reaction mechanism. Why do we believe that only bimolecular collisions and unimolecular decompositions are important in most reaction mechanisms?

66. For the reaction



the rate law is: $\text{Rate} = k[(\text{CH}_3)_3\text{CBr}]$.

Identify each mechanism that is compatible with the rate law.

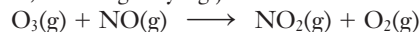
- (a) $(\text{CH}_3)_3\text{CBr} \longrightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$ (slow)
 $(\text{CH}_3)_3\text{C}^+ + \text{OH}^- \longrightarrow (\text{CH}_3)_3\text{COH}$ (fast)
- (b) $(\text{CH}_3)_3\text{CBr} + \text{OH}^- \longrightarrow (\text{CH}_3)_3\text{COH} + \text{Br}^-$
- (c) $(\text{CH}_3)_3\text{CBr} + \text{OH}^- \longrightarrow (\text{CH}_3)_2(\text{CH}_2)\text{CBr}^- + \text{H}_2\text{O}$ (slow)
 $(\text{CH}_3)_2(\text{CH}_2)\text{CBr}^- \longrightarrow (\text{CH}_3)_2(\text{CH}_2)\text{C} + \text{Br}^-$ (fast)
 $(\text{CH}_3)_2(\text{CH}_2)\text{C} + \text{H}_2\text{O} \longrightarrow (\text{CH}_3)_3\text{COH}$ (fast)
67. Write the overall reaction and the rate expressions that correspond to the following reaction mechanisms. Be sure to eliminate intermediates from the answers.

- (a) $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$ (fast, equilibrium)
 $\text{C} + \text{E} \longrightarrow \text{F}$ (slow)
- (b) $\text{A} \rightleftharpoons \text{B} + \text{C}$ (fast, equilibrium)
 $\text{C} + \text{D} \rightleftharpoons \text{E}$ (fast, equilibrium)
 $\text{E} \longrightarrow \text{F}$ (slow)

68. Write the overall reaction and the rate expressions that correspond to the following mechanisms. Be sure to eliminate intermediates from the answers.

- (a) $2\text{A} + \text{B} \rightleftharpoons \text{D}$ (fast, equilibrium)
 $\text{D} + \text{B} \longrightarrow \text{E} + \text{F}$ (slow)
 $\text{F} \longrightarrow \text{G}$ (fast)
- (b) $\text{A} + \text{B} \rightleftharpoons \text{C}$ (fast, equilibrium)
 $\text{C} + \text{D} \rightleftharpoons \text{F}$ (fast, equilibrium)
 $\text{F} \longrightarrow \text{G}$ (slow)

69. The ozone, O_3 , of the stratosphere can be decomposed by reaction with nitrogen oxide (commonly called nitric oxide), NO , from high-flying jet aircraft.



The rate expression is $\text{rate} = k[\text{O}_3][\text{NO}]$. Which of the following mechanisms are consistent with the observed rate expression?

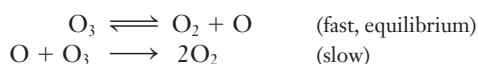
- (a) $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_3 + \text{O}$ (slow)
 $\text{NO}_3 + \text{O} \longrightarrow \text{NO}_2 + \text{O}_2$ (fast)
 $\text{O}_3 + \text{NO} \longrightarrow \text{NO}_2 + \text{O}_2$ (overall)
- (b) $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$ (slow)
 (one step)
- (c) $\text{O}_3 \longrightarrow \text{O}_2 + \text{O}$ (slow)
 $\text{O} + \text{NO} \longrightarrow \text{NO}_2$ (fast)
 $\text{O}_3 + \text{NO} \longrightarrow \text{NO}_2 + \text{O}_2$ (overall)
- (d) $\text{NO} \longrightarrow \text{N} + \text{O}$ (slow)
 $\text{O} + \text{O}_3 \longrightarrow 2\text{O}_2$ (fast)
 $\text{O}_2 + \text{N} \longrightarrow \text{NO}_2$ (fast)
 $\text{O}_3 + \text{NO} \longrightarrow \text{NO}_2 + \text{O}_2$ (overall)
- (e) $\text{NO} \rightleftharpoons \text{N} + \text{O}$ (fast, equilibrium)
 $\text{O} + \text{O}_3 \longrightarrow 2\text{O}_2$ (slow)
 $\text{O}_2 + \text{N} \longrightarrow \text{NO}_2$ (fast)
 $\text{O}_3 + \text{NO} \longrightarrow \text{NO}_2 + \text{O}_2$ (overall)



Charles D. Winters

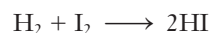
NO_2 sample

70. A proposed mechanism for the decomposition of ozone, $2\text{O}_3 \longrightarrow 3\text{O}_2$, is

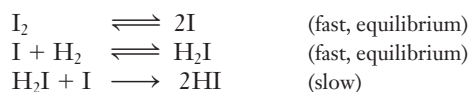


Derive the rate equation for the net reaction.

71. A mechanism for the gas-phase reaction

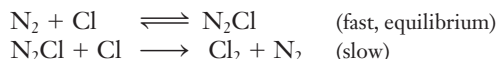


was discussed in the chapter. (a) Show that this mechanism predicts the correct rate law, $\text{rate} = k[\text{H}_2][\text{I}_2]$.



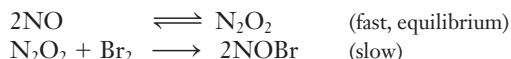
(b) Identify any reaction intermediates in this proposed mechanism.

72. ▲ The combination of Cl atoms is catalyzed by $\text{N}_2(\text{g})$. The following mechanism is suggested.



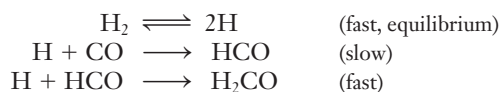
(a) Identify any reaction intermediates in this proposed mechanism. (b) Is this mechanism consistent with the experimental rate law, $\text{rate} = k[\text{N}_2][\text{Cl}]^2$?

73. The reaction between NO and Br_2 was discussed in Section 16-7. The following mechanism has also been proposed.



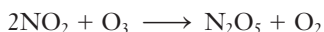
Is this mechanism consistent with the observation that the reaction is second order in NO and first order in Br_2 ?

74. ▲ The following mechanism for the reaction between H_2 and CO to form formaldehyde, H_2CO , has been proposed.

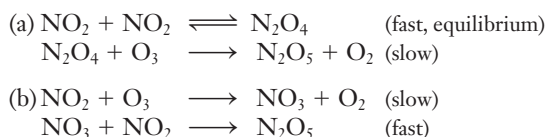


(a) Write the balanced equation for the overall reaction. (b) The observed rate dependence is found to be one-half order in H_2 and first order in CO. Is this proposed reaction mechanism consistent with the observed rate dependence?

75. The reaction between nitrogen dioxide and ozone,



has been studied at 231 K. The experimental rate equation is $\text{rate} = k[\text{NO}_2][\text{O}_3]$. (a) What is the order of the reaction? (b) Is either of the following proposed mechanisms consistent with the given kinetic data? Show how you arrived at your answer.

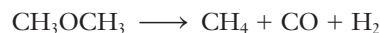


Mixed Exercises

76. (a) What is the transition state in a reaction mechanism? (b) Are the energy of activation and the transition state related concepts? Explain. (c) How does the activation energy affect the rate of reaction?
77. Refer to the reaction and data in Exercise 63. Assume that we begin with 2.80 mol of ClO_2F in a 3.00-L container.

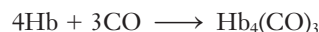
(a) How many moles of ClO_2F would remain after 2.00 minutes at 25°C ? (b) How much time would be required for 99.0% of the ClO_2F to decompose at 25°C ?

78. Refer to the reaction and data in Exercise 64. Assume that we begin with 2.80 mol of N_2O_5 in a 3.00-L container. (a) How many moles of N_2O_5 would remain after 2.00 minutes at 25°C ? (b) How much time would be required for 99.0% of the N_2O_5 to decompose at 25°C ?
79. The decomposition of gaseous dimethyl ether



follows first-order kinetics. Its half-life is 25.0 min at 500°C . (a) Starting with 12.00 g of dimethyl ether at 500°C , how many grams would remain after 150. minutes? (b) In part (a), how many grams would remain after 180. minutes? (c) In part (b), what fraction remains, and what fraction reacts? (d) Calculate the time, in minutes, required to decrease 24.0 mg of dimethyl ether to 2.40 mg.

80. The rate of the hemoglobin (Hb)–carbon monoxide reaction,



has been studied at 20°C . Concentrations are expressed in micromoles per liter ($\mu\text{mol/L}$).

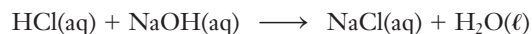
Concentration ($\mu\text{mol/L}$)		Rate of Disappearance of Hb ($\mu\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$)
[Hb]	[CO]	
3.36	1.00	0.941
6.72	1.00	1.88
6.72	3.00	5.64

(a) Write the rate equation for the reaction. (b) Calculate the rate constant for the reaction. (c) Calculate the rate at the instant when $[\text{Hb}] = 1.50$ and $[\text{CO}] = 0.600 \mu\text{mol/L}$.

81. How does an enzyme change the speed with which a reaction reaches equilibrium? Can an enzyme change the final equilibrium concentrations? Explain.

Conceptual Exercises

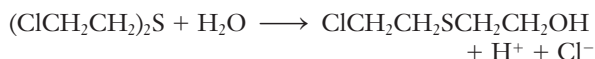
82. Some reactions occur faster than others due to differences in the shapes of the reactants. Use the collision theory to explain these observations.
83. How is it possible for two reactant molecules to collide with the correct orientation and still not react?
84. Write the net ionic equation for the following reaction. Construct a potential energy diagram, like that in Figure 16-10, for this reaction.



85. Starting with only two molecules of each reactant in a reaction that is first order in each reactant, show how the collision theory predicts that the rate of reaction will double if the amount of either reactant is doubled.

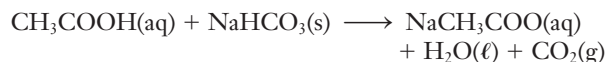


86. A sentence in an introductory chemistry textbook reads, "Dioxygen reacts with itself to form trioxxygen, ozone, according to the following equation, $3\text{O}_2 \longrightarrow 2\text{O}_3$." As a student of chemistry, what would you write to criticize this sentence?
87. A stream of gaseous H_2 is directed onto finely divided platinum powder in the open air. The metal immediately glows white-hot and continues to do so as long as the stream continues. Explain.
88. Is the activation energy of a reaction expected to be higher or lower when the same reactants are in the gaseous state rather than the liquid or solid state? Explain.
89. Construct a diagram like that in Figure 16-10a. (a) Write a generic equation that would have such a potential energy diagram. (b) Is the reaction exothermic or endothermic? (c) Label the energy of activation. It is equal to the difference between what two points on your drawing?
90. Construct a diagram like that in Figure 16-10b. (a) Write a generic equation that would have such a potential energy diagram. (b) Is the reaction exothermic or endothermic? (c) Label the energy of activation. It is equal to the difference between what two points on your drawing?
91. In 1946 W. M. Grant and V. E. Kinsey reported on the rate of hydrolysis of di(2-chloroethyl)sulfide $[(\text{ClCH}_2\text{CH}_2)_2\text{S}]$, commonly known as mustard gas] in aqueous solution:



What are some of the quantities that could be measured to observe the rate of this reaction?

92. When vinegar (5% acetic acid) is added to solid baking soda (sodium hydrogen carbonate), they react to produce sodium acetate, water, and carbon dioxide gas:



List four ways that the rate of this reaction can be increased.

93. According to the collision theory, the rate of a reaction can be expressed as the product of three factors:

$$\text{rate} = \text{collision frequency} \times \text{energy factor} \times \text{probability factor}$$

	factor
rate	number of effective collisions per unit volume per unit time
collision frequency	total number of collisions per unit volume per unit time
energy factor	fraction of the collisions with sufficient energy
probability factor	fraction of collisions with proper orientation

Which of these three factors are most affected by each of the following changes in the reaction conditions or the reacting substances? Increasing the temperature; switching to a similar substance that is a larger, heavier molecule; cutting large solid pieces into much smaller pieces; adding a catalyst; diluting a solution; increasing the pressure of a gas.

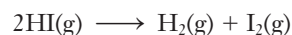
94. Listed below are the equations and the rate law expressions for the gas-phase decompositions of three compounds: N_2O_5 , NO_2 , and NH_3 .

Reaction	Rate Law
$2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$	$\text{rate} = k[\text{N}_2\text{O}_5]$
$2\text{NO}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$	$\text{rate} = k[\text{NO}_2]^2$
$2\text{NH}_3(\text{g}) \xrightarrow{\text{Pt}} \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$	$\text{rate} = k[\text{NH}_3]^2$

For each compound, start with an initial concentration of 0.80 M at 8:00 a.m. and a first half-life of 21 minutes. At what times will the concentration of each starting compound be 0.40 M? 0.20 M? 0.10 M?

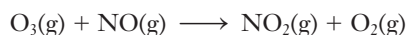
Building Your Knowledge

95. The following explanation of the operation of a pressure cooker appears in a cookbook: "Boiling water in the presence of air can never produce a temperature higher than 212°F , no matter how high the heat source. But in a pressure cooker, the air is withdrawn first, so the boiling water can be maintained at higher temperatures." Support or criticize this explanation.
96. ▲ A cookbook gives the following general guideline for use of a pressure cooker. "For steaming vegetables, cooking time at a gauge pressure of 15 pounds per square inch (psi) is $\frac{1}{3}$ that at atmospheric pressure." Remember that gauge pressure is measured relative to the external atmospheric pressure, which is 15 psi at sea level. From this information, estimate the activation energy for the process of steaming vegetables. (*Hint*: Clausius and Clapeyron may be able to help you.)
97. For most reactions that involve an enzyme, the rate of product formation versus reactant concentration increases as reactant concentration increases until a maximum value is obtained, after which further increases do not yield increased rates. Using a description like that in Figure 16-19, describe how the reaction may be first order with respect to substrate but the amount of enzyme can also be a determining factor.
98. Using the mechanism and relative energy values shown in Figure 16-12, prepare Lewis formulas that illustrate the species that are likely to be present at each of the peaks and troughs in the graphical representation given in Figure 16-12. (*Hint*: You may need to label some bonds as being weaker, stretched, in the process of being formed, and so on.)
99. The activation energy for the reaction



is 179 kJ/mol. Based upon Figure 16-12, construct a diagram for this multistep reaction. (*Hint*: Calculate ΔH^0 from values in Appendix K. How does ΔH^0 compare with ΔE for this reaction?) Show energy values if known.

100. ▲ The activation energy for the reaction between O_3 and NO is 9.6 kJ/mol.



(a) Use the thermodynamic quantities in Appendix K to calculate ΔH° for this reaction. (b) Prepare an activation energy plot similar to that in Figure 16-10 for this reaction. (*Hint:* How does ΔH° compare with ΔE for this reaction?)

Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

101. Go to en.wikipedia.org/wiki/Arrhenius_equation or another website and locate information on the Arrhenius equation. For a particular reaction, how could one determine the value of A in the Arrhenius equation for that reaction?
101. Go to www.chemguide.co.uk/physical/basicrates/arrhenius.html or another website and locate information on the Arrhenius equation. Describe a reaction found at this website that follows a first-order mechanism.
103. Use the *Handbook of Chemistry and Physics* or a website and locate information on kinetics, conversion factors, or rate constants. Which of the units for a second-order reaction found in this handbook or on another website is/are equivalent to the units used in this textbook?
104. Between 1957 and 1990, according to NASA, the average amount of ozone in the stratosphere dropped from about 320 to about 130 Dobson Units (a measure of thickness). In a very blunt calculation, the annual percentage drop over this period can be calculated as the quantity $[(320 - 130) / 320]$ divided by $[1990 - 1957]$. The 2007 CDC statistics show that 58,094 Americans were diagnosed with cancerous skin melanomas that year. If the annual percent drop in ozone concentration calculated above held steady, how many additional new cases of skin cancer in the U.S. would have resulted for 2008 as a result of the drop?
105. Before the late 1920s (when Freon was invented), household refrigerators commonly ran on ammonia (NH_3) or sulfur dioxide (SO_2) gases. If you aren't already familiar with them, do a quick search on the safety hazards of these compounds. Would you rather have one of these old appliances in your kitchen, or a CFC-based fridge? Does your choice introduce conflict between what's best for the immediate environment and what's best for the global environment?
106. Another fluorinated hydrocarbon sold by DuPont is a common product you probably have in your home. What is it? (*Hint:* You won't stick to it.)



Chemical Equilibrium

17



Chemical equilibrium plays an important role in the operation of chemical plants where manufacturers want to optimize the amount of product. This can be done by adjusting reaction conditions such as temperature, pressure, and concentrations of reactants used, all key factors that affect chemical equilibrium.

littlwormy/Shutterstock.com

OUTLINE

- 17-1** Basic Concepts
- 17-2** The Equilibrium Constant
- 17-3** Variation of K_c with the Form of the Balanced Equation
- 17-4** The Reaction Quotient
- 17-5** Uses of the Equilibrium Constant, K_c
- 17-6** Disturbing a System at Equilibrium: Predictions
- 17-7** The Haber Process:
A Commercial Application of Equilibrium
- 17-8** Disturbing a System at Equilibrium: Calculations
- 17-9** Partial Pressures and the Equilibrium Constant
- 17-10** Relationship Between K_p and K_c
- 17-11** Heterogeneous Equilibria
- 17-12** Relationship Between ΔG_{rxn}^0 and the Equilibrium Constant
- 17-13** Evaluation of Equilibrium Constants at Different Temperatures

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Explain the basic ideas of chemical equilibrium
- ▶ Explain what an equilibrium constant is and what it tells us
- ▶ Explain what a reaction quotient is and what it tells us
- ▶ Use equilibrium constants to describe systems at equilibrium
- ▶ Recognize the factors that affect equilibria and predict the resulting effects
- ▶ Use the equilibrium constant expressed in terms of partial pressures (K_p) and relate K_p to K_c
- ▶ Describe heterogeneous equilibria and write their equilibrium constants
- ▶ Use the relationships between thermodynamics and equilibrium
- ▶ Estimate equilibrium constants at different temperatures

17-1 Basic Concepts

Chemical reactions that can occur in either direction are called **reversible reactions**. Most reversible reactions do not go to completion. That is, even when reactants are mixed in stoichiometric quantities, they are not completely converted to products.

Reversible reactions can be represented in general terms as follows, where the capital letters represent formulas and the lowercase letters represent the stoichiometric coefficients in the balanced equation.



The double arrow ($\rightleftharpoons$) indicates that the reaction is reversible—that is, both the forward and reverse reactions occur simultaneously. In discussions of chemical equilibrium, the substances that appear on the left side of the balanced chemical equation are called the “reactants,” and those on the right side are called the “products.” In fact, the reaction can proceed in *either direction*. When A and B react to form C and D at the *same rate* at which C and D react to form A and B, the system is at *equilibrium*.

Chemical equilibrium exists when two opposing reactions occur simultaneously at the same rate.

▶ The dynamic nature of chemical equilibrium can be proved experimentally by inserting radioactive atoms into a small percentage of reactant or product molecules. Even when the initial mixture is at equilibrium, radioactive atoms eventually appear both in reactant and in product molecules.

S TOP & THINK

In Chapter 7 the single line with an arrowhead on each end $\leftrightarrow$ was introduced as a way of indicating resonance. We do not use it to indicate that a reaction is reversible. The double arrow $\rightleftharpoons$ is used to indicate a reversible reaction or an equilibrium.

Chemical equilibria are **dynamic equilibria**; that is, individual molecules are continually reacting, even though the overall composition of the reaction mixture does not change. In a system at equilibrium, the equilibrium is said to lie toward the right if more C and D are present than A and B (product-favored), and to lie toward the left if more A and B are present (reactant-favored).

Consider a case in which the coefficients in the equation for a reaction are all 1. When substances A and B react, the rate of the forward reaction decreases as time passes because the concentrations of A and B decrease.



As the concentrations of C and D build up, they start to re-form A and B.



As more C and D molecules are formed, more can react, and so the rate of reaction between C and D increases with time. Eventually, the two reactions occur at the same rate, and the system is at equilibrium (Figure 17-1).



If a reaction begins with only C and D present, the rate of reaction (2) decreases with time, and the rate of reaction (1) increases with time until the two rates are equal.

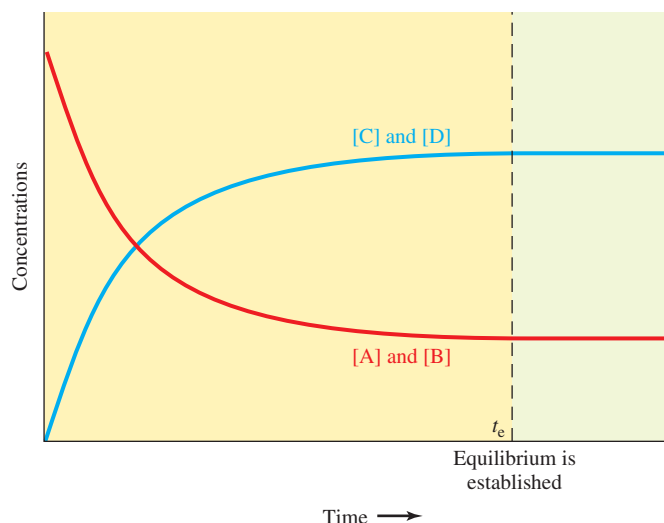
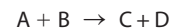


Figure 17-1 Variation in the concentrations of species present in the $A + B \rightleftharpoons C + D$ system as equilibrium is approached, beginning with equal concentrations of A and B only. For this reaction, production of products is favored. As we will see, this corresponds to a value of the equilibrium constant greater than 1. Brackets, [], represent the concentration, in moles per liter, of the species enclosed within them. The time axis may be in any convenient units—seconds, minutes, hours, and so on.

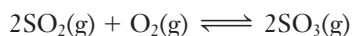
► Whether or not a reaction has reached equilibrium, chemists often use a single reaction arrow as a shortcut:



The single reaction arrow does not necessarily mean that the reaction is not at equilibrium or that it goes completely to products. In this text, we are careful to show the equilibrium arrows $\rightleftharpoons$ when we wish to emphasize a reaction at equilibrium, as throughout Chapters 17 through 20.

The $\text{SO}_2\text{--O}_2\text{--SO}_3$ System

Consider the reversible reaction of sulfur dioxide with oxygen to form sulfur trioxide at 1500 K.



Suppose 0.400 mole of SO_2 and 0.200 mole of O_2 are injected into a closed 1.00-liter container. When equilibrium is established (at time t_e , Figure 17-2a), we find that 0.056 mole of SO_3 has formed and that 0.344 mole of SO_2 and 0.172 mole of O_2 remain unreacted. The amount of product at equilibrium does not increase further if the reaction is given additional time. These changes are summarized in the following reaction summary, using molarity units rather than moles. (They are numerically identical here because the volume of the reaction vessel is 1.00 liter.) The changes due to reaction are represented by the *changes* in concentrations.

	$2\text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$	$\rightleftharpoons$	$2\text{SO}_3(\text{g})$
initial conc'n	0.400 M		0.200 M		0
change due to rxn	−0.056 M		−0.028 M		+0.056 M
equilibrium conc'n	0.344 M		0.172 M		0.056 M

In a similar experiment, 0.500 mole of SO_3 is introduced alone into a closed 1.00-liter container. This time the reaction proceeds from *right to left* as the equation is written. The *changes in concentration* are in the same 2:1:2 ratio as in the previous case, as required by the coefficients of the balanced equation. The time required to reach equilibrium may be longer or shorter. When equilibrium is established (at time t_e , Figure 17-2b), 0.076 mole of SO_3 , 0.212 mole of O_2 , and 0.424 mole of SO_2 are present. These equilibrium amounts differ from those in the previous case, but they are related in an important way, as we will see in the next section.

	$2\text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$	$\rightleftharpoons$	$2\text{SO}_3(\text{g})$
initial conc'n	0		0		0.500 M
change due to rxn	+0.424 M		+0.212 M		−0.424 M
equilibrium conc'n	0.424 M		0.212 M		0.076 M

The results of these experiments are summarized in the following table and in Figure 17-2.

	Initial Concentrations			Equilibrium Concentrations		
	$[\text{SO}_2]$	$[\text{O}_2]$	$[\text{SO}_3]$	$[\text{SO}_2]$	$[\text{O}_2]$	$[\text{SO}_3]$
Experiment 1	0.400 M	0.200 M	0 M	0.344 M	0.172 M	0.056 M
Experiment 2	0 M	0 M	0.500 M	0.424 M	0.212 M	0.076 M

Unless otherwise noted, all content on this page is © Cengage Learning.

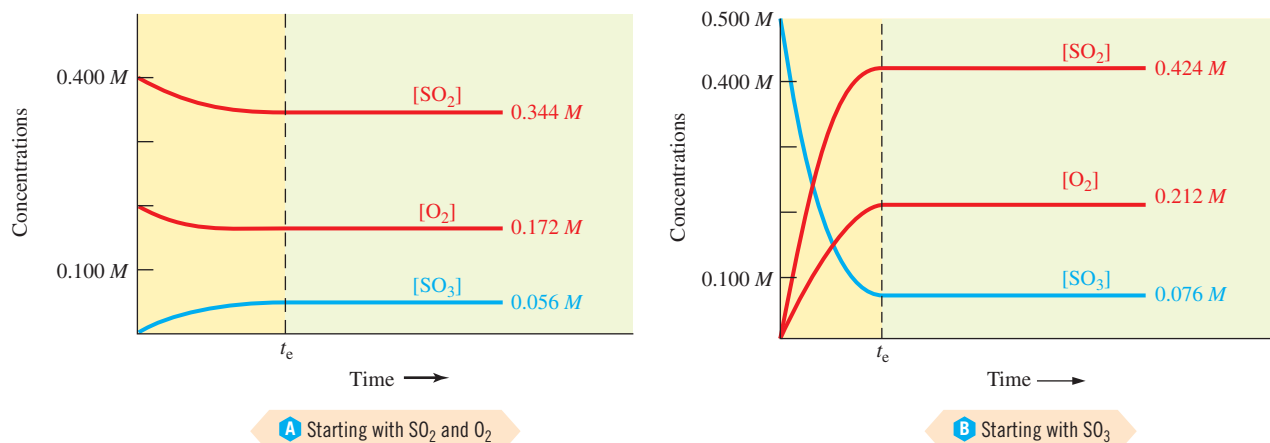
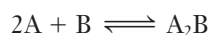


Figure 17-2 Establishment of equilibrium in the $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ system. (a) Beginning with stoichiometric amounts of SO_2 and O_2 and no SO_3 . (b) Beginning with only SO_3 and no SO_2 or O_2 . Greater changes in concentrations occur to establish equilibrium when starting with SO_3 than when starting with SO_2 and O_2 . The equilibrium favors SO_2 and O_2 .

17-2 The Equilibrium Constant

Suppose a reversible reaction occurs by a single elementary reaction step:



The rate of the forward reaction is $\text{rate}_f = k_f[\text{A}]^2[\text{B}]$; the rate of the reverse reaction is $\text{rate}_r = k_r[\text{A}_2\text{B}]$. In these expressions, k_f and k_r are the *specific rate constants* of the forward and reverse reactions, respectively. By definition, the two rates are equal *at equilibrium* ($\text{rate}_f = \text{rate}_r$). So we write

$$k_f[\text{A}]^2[\text{B}] = k_r[\text{A}_2\text{B}] \quad (\text{at equilibrium})$$

Dividing both sides of this equation by k_r and by $[\text{A}]^2[\text{B}]$ gives

$$\frac{k_f}{k_r} = \frac{[\text{A}_2\text{B}]}{[\text{A}]^2[\text{B}]}$$

At any specific temperature, both k_f and k_r are constants, so k_f/k_r is also a constant.

This ratio is given a special name and symbol, the *equilibrium constant*, K_c or simply K .

$$K_c = \frac{[\text{A}_2\text{B}]}{[\text{A}]^2[\text{B}]} \quad (\text{at equilibrium})$$

We can show that even if the overall reaction occurs by a multistep mechanism, the equilibrium constant is the product and ratio of the rate constants for each step of the mechanism. Regardless of the mechanism by which any reaction occurs, the concentrations of reaction intermediates cancel out and the equilibrium constant expression for the reaction has the same form. For a reaction in general terms, the equilibrium constant can always be written as follows:

$$\text{For } \underbrace{a\text{A} + b\text{B}}_{\text{reactants}} \rightleftharpoons \underbrace{c\text{C} + d\text{D}}_{\text{products}}, \quad K_c = \frac{\overbrace{[\text{C}]_{\text{eq}}^c [\text{D}]_{\text{eq}}^d}^{\text{product concentrations}}}{\underbrace{[\text{A}]_{\text{eq}}^a [\text{B}]_{\text{eq}}^b}_{\text{reactant concentrations}}}$$

STOP & THINK

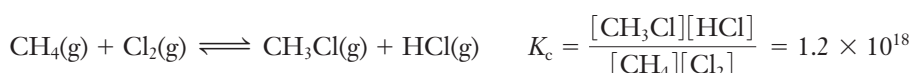
Remember that for *elementary* (or *fundamental*) reactions the coefficients do correspond to the orders of the reactant and product concentrations.

► The subscript c refers to concentrations. The brackets, [], in this expression indicate *equilibrium concentrations* in moles per liter.

The **equilibrium constant**, K_c , is defined as the product of the *equilibrium concentrations* (in moles per liter) of the products, each raised to the power that corresponds to its coefficient in the balanced equation, divided by the product of the *equilibrium concentrations* of reactants, each raised to the power that corresponds to its coefficient in the balanced equation.

► Moles per liter is equal to molarity (M) or molar concentration.

Numerical values for K_c can be determined from experiments or from thermodynamic data (see Section 17-12). Some equilibrium constant expressions and their numerical values at 25°C are



► You must remember that the concentrations in the equilibrium constant expression are those at equilibrium.

Remember that calculations with K_c values always involve *equilibrium values* of concentrations.

The thermodynamic definition of the equilibrium constant involves activities rather than concentrations. The **activity** of a component of an ideal mixture is the ratio of its concentration or partial pressure to a standard concentration (1 M for solutions) or a standard pressure (1 atm for gases). For now, we can consider the activity of each species to be a dimensionless quantity whose numerical value can be determined as follows.

1. For any pure liquid or pure solid, the activity is taken as 1 (by definition).
2. For components of ideal solutions, the activity of each component is taken to be the ratio of its molar concentration to a standard concentration of 1 M , so the units cancel.
3. For gases in an ideal mixture, the activity of each component is taken to be the ratio of its partial pressure to a standard pressure of 1 atm, so again the units cancel.

► You can think of the activity as the molar concentration of a solution component or the partial pressure of a gas with the units omitted.

Because of the use of activities, *the equilibrium constant has no units; the values we put into K_c are numerically equal to molar concentrations but are dimensionless*, that is, they have no units. Therefore, calculations involving equilibrium are frequently carried out without units; we will follow that practice in this text.

The magnitude of K_c is a measure of the extent to which reaction occurs. For any balanced chemical equation, the value of K_c

1. is always the same at a given temperature.
2. changes if the temperature changes.
3. does not depend on the initial concentrations.

STOP & THINK
These are three very important ideas.

A value of K_c *much* greater than 1 indicates that the “numerator concentrations” (products) would be much greater than the “denominator concentrations” (reactants); this means that at equilibrium most of the reactants would be converted into products. For example, the reaction $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$ shown earlier goes nearly to completion; earlier in this chapter and in Chapter 15, we called such a reaction spontaneous or “product-favored.” On the other hand, if K_c is quite small, equilibrium is established when most of the reactants remain unreacted and only small amounts of products are formed. The reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ shown earlier reaches equilibrium with only a tiny amount of NO present; earlier in this chapter and in Chapter 15, we called such a reaction nonspontaneous or “reactant-favored.”

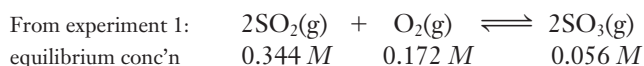
For a given chemical reaction at a specific temperature, the product of the concentrations of the products formed by the reaction, each raised to the appropriate power, divided

Unless otherwise noted, all content on this page is © Cengage Learning.

► In the K_c expression, the power for each reactant and product is equal to its coefficient in the balanced chemical equation. Remember, however, that pure solids and liquids have activities = 1 and do not appear in the equilibrium expression.

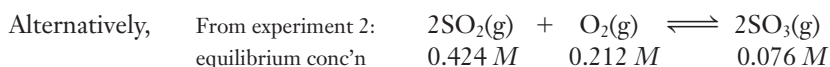
by the product of the concentrations of the reactants, each raised to the appropriate power, always has the same value, that is, K_c . This does *not* mean that the individual equilibrium concentrations for a given reaction are always the same, but it does mean that this particular numerical combination of their values (K_c) is constant.

Consider again the $\text{SO}_2\text{—O}_2\text{—SO}_3$ equilibrium described in Section 17-1. We can use the *equilibrium* concentrations from either experiment to calculate the value of the equilibrium constant for this reaction at 1500 K.



Substituting the numerical values (without units) into the equilibrium expression gives the value of the equilibrium constant.

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(0.056)^2}{(0.344)^2(0.172)} = 0.15$$



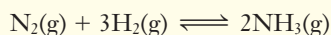
$$K_c = \frac{(0.076)^2}{(0.424)^2(0.212)} = 0.15$$

No matter what combinations of reactant and product concentrations we start with, the resulting *equilibrium* concentrations at 1500 K for this reversible reaction would always give the same value of K_c , 0.15.

For the reversible reaction written *as it is* with SO_2 and O_2 shown as reactants and SO_3 shown as the product, K_c is 0.15 at 1500 K.

EXAMPLE 17-1 Calculation of K_c

Some nitrogen and hydrogen are placed in an empty 5.00-liter container at 500°C. When equilibrium is established, 3.01 mol of N_2 , 2.10 mol of H_2 , and 0.565 mol of NH_3 are present. Evaluate K_c for the following reaction at 500°C.



Plan

We find the *equilibrium concentrations* by dividing the number of moles of each reactant and product by the volume, 5.00 liters. Then we substitute these equilibrium concentrations into the equilibrium constant expression.

Solution

The equilibrium concentrations are

$$\begin{aligned} [\text{N}_2] &= 3.01 \text{ mol}/5.00 \text{ L} = 0.602 \text{ M} \\ [\text{H}_2] &= 2.10 \text{ mol}/5.00 \text{ L} = 0.420 \text{ M} \\ [\text{NH}_3] &= 0.565 \text{ mol}/5.00 \text{ L} = 0.113 \text{ M} \end{aligned}$$

We substitute these numerical values into the expression for K_c .

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.113)^2}{(0.602)(0.420)^3} = 0.286$$

Thus, for the reaction of N_2 and H_2 to form NH_3 at 500°C, we can write

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 0.286$$

► Remember that the concentrations in K_c calculations are equilibrium values of molar concentration. But, since we should be using activities, which have no units, we do not carry concentration units along in the calculation.

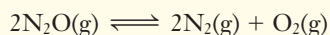
The value of K_c from Example 17-1 is much different from the value given earlier for the same reaction at 25°C. For this reaction, products are favored at the lower temperature ($K_c = 3.6 \times 10^8$ at 25°C), whereas reactants are favored at the higher temperature ($K_c = 0.286$ at 500°C). You may recall from Chapter 16 that the rate constant, k , for any reaction increases with increasing temperature. But the value of K_c for different reactions responds differently to temperature changes; for some reactions, K_c increases with increasing temperature, whereas for others K_c decreases with increasing temperature, as we will see in Sections 17-6 and 17-13.

STOP & THINK

The small value of K_c indicates that the equilibrium lies to the left, that is, the *forward* reaction is nonspontaneous (reactant-favored).

EXAMPLE 17-2 Calculation of K_c

We put 10.0 moles of N_2O into a 2.00-L container at some temperature, where it decomposes according to



At equilibrium, 2.20 moles of N_2O remain. Calculate the value of K_c for the reaction.

Plan

We express all concentrations in moles per liter. The mole ratio from the balanced chemical equation allows us to find the *changes* in concentrations of the other substances in the reaction. We use the reaction summary to find the equilibrium concentrations to use in the K_c expression.

Solution

At equilibrium, 2.20 mol N_2O remain, so

$$\begin{aligned} \underline{x} \text{ mol } N_2O \text{ reacting} &= 10.00 \text{ mol } N_2O \text{ initial} - 2.20 \text{ mol } N_2O \text{ remaining} \\ &= 7.80 \text{ mol } N_2O \text{ reacting} \end{aligned}$$

The initial $[N_2O] = (10.00 \text{ mol})/(2.00 \text{ L}) = 5.00 \text{ M}$; the concentration of N_2O that reacts is $(7.80 \text{ mol})/(2.00 \text{ L}) = 3.90 \text{ M}$. From the balanced chemical equation, each 2 mol N_2O that react produces 2 mol N_2 and 1 mol O_2 , or a reaction ratio of

$$1 \text{ mol } N_2O \text{ reacting} : 1 \text{ mol } N_2 \text{ formed} : \frac{1}{2} \text{ mol } O_2 \text{ formed}$$

We can now write the reaction summary.

	$2N_2O(g)$	$\rightleftharpoons$	$2N_2(g)$	+	$O_2(g)$
initial	5.00 M		0		0
change due to rxn	-3.90 M		+3.90 M		$+\frac{1}{2}(3.90)$
					= 1.95 M
equilibrium	1.10 M		3.90 M		1.95 M

We put these equilibrium concentrations into the equilibrium constant expression and evaluate K_c .

$$K_c = \frac{[N_2]^2[O_2]}{[N_2O]^2} = \frac{(3.90)^2(1.95)}{(1.10)^2} = 24.5$$

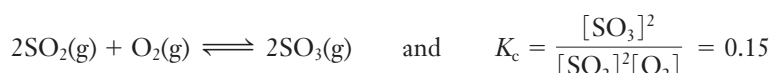
You should now work Exercises 24 and 28.

STOP & THINK

Remember that concentrations appear with no units in equilibrium calculations.

17-3 Variation of K_c with the Form of the Balanced Equation

The numerical value of K_c depends on how we write the balanced equation for the reaction. We wrote the equation for the reaction of SO_2 and O_2 to produce SO_3 , and its equilibrium constant expression as



STOP & THINK

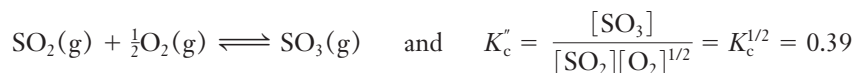
Reversing an equation is the same as multiplying all coefficients by -1 . This reverses the roles of "reactants" and "products."

Suppose we write the equation for the same reaction in reverse. The equation and its equilibrium constant, written this way, are



We see that K'_c , the equilibrium constant for the equation written in reverse, is the *reciprocal* of K_c , the equilibrium constant for the original equation.

If the reaction is divided by a factor of 2, the new equilibrium expression is then written as:

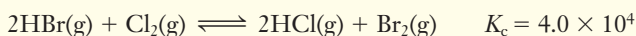


► We see that K''_c is the square root of K_c . $K_c^{1/2}$ means the square root of K_c .

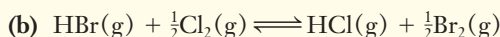
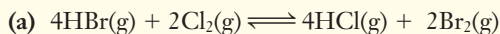
If an equation for a reaction is multiplied by any factor, n , then the original value of K_c is raised to the n th power. Thus, we must always know the balanced chemical equation that corresponds to the value of K_c for a chemical reaction.

EXAMPLE 17-3 Variation of the Form of K_c

You are given the following chemical equation and its equilibrium constant at a given temperature.



Write the expression for the equilibrium constant and calculate its numerical value for each of the following at the same temperature.



► A coefficient of $\frac{1}{2}$ refers to $\frac{1}{2}$ of a mole, *not* $\frac{1}{2}$ of a molecule.

Plan

We recall the definition of the equilibrium constant. For the original equation,

$$K_c = \frac{[\text{HCl}]^2[\text{Br}_2]}{[\text{HBr}]^2[\text{Cl}_2]} = 4.0 \times 10^4$$

Solution

(a) The original equation has been multiplied by 2, so K_c must be squared.

$$K'_c = \frac{[\text{HCl}]^4[\text{Br}_2]^2}{[\text{HBr}]^4[\text{Cl}_2]^2} \quad K'_c = (K_c)^2 = (4.0 \times 10^4)^2 = 1.6 \times 10^9$$

(b) The original equation has been multiplied by $\frac{1}{2}$ (divided by 2), so K_c must be raised to the $\frac{1}{2}$ power. The value of K'_c is the square root of the original K_c value.

$$K''_c = \frac{[\text{HCl}][\text{Br}_2]^{1/2}}{[\text{HBr}][\text{Cl}_2]^{1/2}} = \sqrt{K_c} = \sqrt{4.0 \times 10^4} = 2.0 \times 10^2$$

You should now work Exercise 30.

17-4 The Reaction Quotient

► The reaction quotient is sometimes called the **mass action expression**.

The **reaction quotient**, Q , for the general reaction is given as follows.

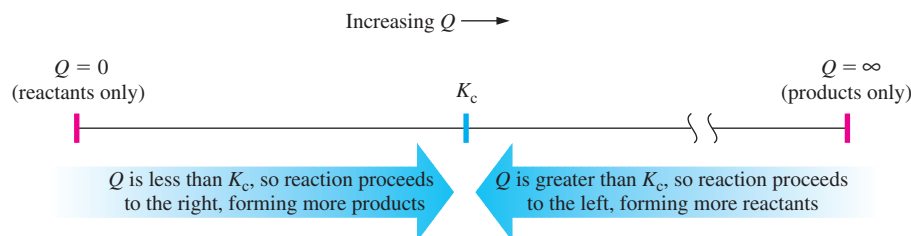
$$\text{For } a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}, \quad Q = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \quad \leftarrow \begin{array}{l} \text{not necessarily} \\ \text{equilibrium} \\ \text{concentrations} \end{array}$$

The reaction quotient has the same *form* as the equilibrium constant, but it involves specific values that are not *necessarily* equilibrium concentrations. If they *are* equilibrium concentrations, then $Q = K_c$. The concept of the reaction quotient is very useful. We can compare the magnitude of Q for any specified mixture of reactants and products with that of K_c for a reaction under given conditions to decide whether the forward or the reverse reaction must occur to a greater extent to establish equilibrium.

We can think of the reaction quotient, Q , as a measure of the progress of the reaction. When the mixture contains *only* reactants, the concentrations in the numerator are zero, so $Q = 0$. As the reaction proceeds to the right, the product concentrations (numerator) increase and the reactant concentrations (denominator) decrease, so Q would increase to an infinitely large value when all reactants have been consumed and only products remain. The value of K_c is a particular value of Q that represents equilibrium mixtures for the reaction.

If for any mixture $Q < K_c$, the forward reaction would occur to a greater extent than the reverse reaction for equilibrium to be established. This is because when $Q < K_c$, the numerator of Q is too small and the denominator is too large. To increase the numerator and to reduce the denominator, A and B must react to produce C and D. Conversely, if $Q > K_c$, the reverse reaction would occur to a greater extent than the forward reaction for equilibrium to be reached. When the value of Q reaches the value of K_c , the system is at equilibrium, so no further *net* reaction occurs.

► When the forward reaction occurs to a greater extent than the reverse reaction, we say that a *net forward* reaction has occurred.



$Q < K_c$ Forward reaction predominates until equilibrium is established.
 $Q = K_c$ System is at equilibrium.
 $Q > K_c$ Reverse reaction predominates until equilibrium is established.

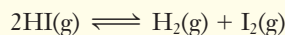
STOP & THINK

Once the balanced chemical equation is written, the substances on the left are called reactants and the ones on the right are products, no matter which way the reaction proceeds.

In Example 17-4 we calculate the value of Q and compare it with the *known* value of K_c to predict the direction of the reaction that leads to equilibrium.

EXAMPLE 17-4 The Reaction Quotient

At a very high temperature, $K_c = 65.0$ for the following reaction.



The following concentrations were detected in a mixture. Is the system at equilibrium? If not, in which direction must the reaction proceed for equilibrium to be established?

$$[\text{HI}] = 0.500 \text{ M}, \quad [\text{H}_2] = 2.80 \text{ M}, \quad \text{and} \quad [\text{I}_2] = 3.40 \text{ M}$$

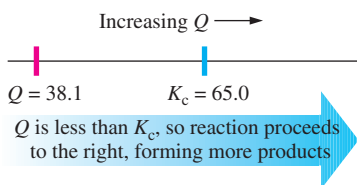
Plan

We substitute these concentrations into the expression for the reaction quotient to calculate Q . Then we compare Q with K_c to see whether the system is at equilibrium.

Solution

$$Q = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(2.80)(3.40)}{(0.500)^2} = 38.1$$

► These concentrations could be present if we started with a mixture of HI, H_2 , and I_2 .



► The equilibrium constant is a “constant” only if the temperature does not change.

But $K_c = 65.0$, so $Q < K_c$. The system is *not* at equilibrium. For equilibrium to be established, the value of Q must *increase* until it equals K_c . This can occur only if the numerator *increases* and the denominator *decreases*. Thus, the forward (left-to-right) reaction must occur to a greater extent than the reverse reaction; that is, some HI must react to form more H_2 and I_2 to reach equilibrium.

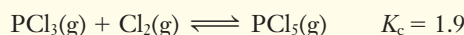
You should now work Exercises 38, 40, and 42.

17-5 Uses of the Equilibrium Constant, K_c

We have seen (Section 17-2) how to calculate the value of K_c from one set of equilibrium concentrations. Once that value has been obtained, the process can be turned around to calculate equilibrium *concentrations* from the equilibrium *constant*.

EXAMPLE 17-5 Finding Equilibrium Concentrations

- (a) The equation for the following reaction and the value of K_c at a given temperature are given. An equilibrium mixture in a 1.00-liter container contains 0.25 mol of PCl_5 and 0.16 mol of PCl_3 . What equilibrium concentration of Cl_2 must be present?



- (b) Suppose the chemical equation had been written as $2PCl_3(g) + 2Cl_2(g) \rightleftharpoons 2PCl_5(g)$. Write the expression for the equilibrium constant for the equation written in this way, and calculate its value.
- (c) Using the same starting amounts as in (a), calculate the equilibrium concentration of Cl_2 .

Plan

We write the equilibrium constant expression and its value. Only one term, $[Cl_2]$, is unknown. We solve for it.

Solution

- (a) Because the volume of the container is 1.00 liter, the molar concentration (mol/L) of each substance is numerically equal to the number of moles. The equilibrium constant expression and its numeric value are

$$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]} = 1.9$$

$$[Cl_2] = \frac{[PCl_5]}{K_c[PCl_3]} = \frac{(0.25)}{(1.9)(0.16)} = 0.82 \text{ M}$$

- (b) We saw in Section 17-3 that multiplying the chemical equation by 2 results in the value of K_c being squared. Thus for the equation $2PCl_3 + 2Cl_2 \rightleftharpoons 2PCl_5$, we have:

$$K_c' = \frac{[PCl_5]^2}{[PCl_3]^2[Cl_2]^2} = 1.9^2 = 3.6$$

- (c) We insert the known equilibrium concentration values from (a) into the expression for K_c' and solve for the equilibrium concentration of $[Cl_2]$.

$$K_c' = \frac{[PCl_5]^2}{[PCl_3]^2[Cl_2]^2} = 3.6$$

$$[Cl_2]^2 = \frac{[PCl_5]^2}{K_c'[Cl_2]^2} = \frac{(0.25)^2}{(3.61)(0.16)^2} = 0.68$$

$$[Cl_2] = 0.82 \text{ M}$$

This is the same concentration that we calculated in (a). Correct equilibrium concentrations can be calculated from any representation of the balanced chemical equation, so long as we treat the equilibrium constant expression and its value in a consistent manner, as shown in Section 17-3.

STOP & THINK

When the value of K_c and the equilibrium values of all but one concentration are known, the unknown concentration can be found.

Often we know the starting concentrations and want to know how much of each reactant and each product would be present at equilibrium. The next two examples illustrate this important kind of calculation.

EXAMPLE 17-6 Finding Equilibrium Concentrations

For the following reaction, the equilibrium constant is 49.0 at a certain temperature. If 0.400 mol each of A and B are placed in a 2.00-liter container at that temperature, what concentrations of all species are present at equilibrium?



Plan

First we find the initial concentrations. Then we write the reaction summary and represent the equilibrium concentrations algebraically. Finally we substitute the algebraic representations of equilibrium concentrations into the K_c expression and find the equilibrium concentrations.

Solution

The initial concentrations are

$$[A] = \frac{0.400 \text{ mol}}{2.00 \text{ L}} = 0.200 \text{ M} \quad [C] = 0 \text{ M}$$

$$[B] = \frac{0.400 \text{ mol}}{2.00 \text{ L}} = 0.200 \text{ M} \quad [D] = 0 \text{ M}$$

We know that the reaction can only proceed to the right because only “reactants” are present. The reaction summary includes the values, or symbols for the values, of (1) initial concentrations, (2) changes in concentrations, and (3) concentrations at equilibrium.

Let x = moles per liter of A that react; then x = moles per liter of B that react and x = moles per liter of C and of D that are formed.

	A	+	B	$\rightleftharpoons$	C	+	D
initial	0.200 M		0.200 M		0 M		0 M
change due to rxn	$-x \text{ M}$		$-x \text{ M}$		$+x \text{ M}$		$+x \text{ M}$
at equilibrium	$(0.200 - x) \text{ M}$		$(0.200 - x) \text{ M}$		$x \text{ M}$		$x \text{ M}$

Now K_c is known, but concentrations are not. But the equilibrium concentrations have all been expressed in terms of the single variable x . We substitute the equilibrium concentrations (*not* the initial ones) into the K_c expression and solve for x .

$$K_c = \frac{[C][D]}{[A][B]} = 49.0$$

$$\frac{(x)(x)}{(0.200 - x)(0.200 - x)} = \frac{x^2}{(0.200 - x)^2} = 49.0$$

This quadratic equation has a perfect square on both sides. We solve it by taking the square roots of both sides of the equation and then rearranging for x .

$$\frac{x}{0.200 - x} = 7.00$$

$$x = 1.40 - 7.00x \quad 8.00x = 1.40 \quad x = \frac{1.40}{8.00} = 0.175$$

Now we know the value of x , so the equilibrium concentrations are

$$[A] = (0.200 - x) \text{ M} = 0.025 \text{ M}; \quad [C] = x \text{ M} = 0.175 \text{ M};$$

$$[B] = (0.200 - x) \text{ M} = 0.025 \text{ M}; \quad [D] = x \text{ M} = 0.175 \text{ M}$$

► We have represented chemical formulas by single letters to simplify the notation in these calculations.

► The coefficients in the equation are all 1's, so the reaction ratio must be 1:1:1:1.

STOP & THINK

We see that the equilibrium concentrations of products are much greater than those of reactants because K_c is much greater than 1.

To check our answers, we use the equilibrium concentrations to calculate Q and verify that its value is equal to K_c .

$$Q = \frac{[C][D]}{[A][B]} = \frac{(0.175)(0.175)}{(0.025)(0.025)} = 49 \quad \text{Recall that } K_c = 49.0$$

The ideas developed in Example 17-6 may also be applied to cases in which the reactants are mixed in nonstoichiometric amounts. This is shown in Example 17-7.

EXAMPLE 17-7 Finding Equilibrium Concentrations

Consider the same system as in Example 17-6 at the same temperature. If 0.600 mol of A and 0.200 mol of B are mixed in a 2.00-liter container and allowed to reach equilibrium, what are the equilibrium concentrations of all species?

Plan

We proceed as we did in Example 17-6. The only difference is that now we have *nonstoichiometric* starting amounts of reactants.

Solution

As in Example 17-6, we let $x = \text{mol/L}$ of A that react; then $x = \text{mol/L}$ of B that react, and $x = \text{mol/L}$ of C and D formed.

	A	+	B	$\rightleftharpoons$	C	+	D
initial	0.300 M		0.100 M		0 M		0 M
change due to rxn	$-x M$		$-x M$		$+x M$		$+x M$
equilibrium	$(0.300 - x) M$		$(0.100 - x) M$		$x M$		$x M$

The initial concentrations are governed by the amounts of reactants mixed together. But *changes in concentrations* due to reaction must still occur in the 1:1:1:1 ratio required by the coefficients in the balanced equation.

► The denominator of this equation is *not* a perfect square, so a different algebraic approach is required.

$$K_c = \frac{[C][D]}{[A][B]} = 49.0 \quad \text{so} \quad \frac{(x)(x)}{(0.300 - x)(0.100 - x)} = 49.0$$

We can arrange this quadratic equation into the standard form, $ax^2 + bx + c = 0$.

$$\begin{aligned} \frac{x^2}{0.0300 - 0.400x + x^2} &= 49.0 \\ x^2 &= 1.47 - 19.6x + 49.0x^2 \\ 48.0x^2 - 19.6x + 1.47 &= 0 \end{aligned}$$

Quadratic equations can be solved by use of the quadratic formula.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this case $a = 48.0$, $b = -19.6$, and $c = 1.47$. Substituting these values gives

$$\begin{aligned} x &= \frac{-(-19.6) \pm \sqrt{(-19.6)^2 - 4(48.0)(1.47)}}{2(48.0)} \\ &= \frac{19.6 \pm 10.1}{96.0} = 0.309 \quad \text{or} \quad 0.099 \end{aligned}$$

Evaluating the quadratic formula always yields two roots. One root (the answer) has physical meaning. The other root, though mathematically correct, is extraneous; that is, it has no physical meaning. The value of x is defined as the number of moles of A per liter that react and the number of moles of B per liter that react. No more B can be consumed than was initially present (0.100 M), so $x = 0.309$ is the extraneous root. Thus, $x = 0.099$ is the root that has physical meaning. The equilibrium concentrations are

$$[A] = (0.300 - x) M = 0.201 M; \quad [B] = (0.100 - x) M = 0.001 M;$$

$$[C] = [D] = x M = 0.099 M$$

You should now work Exercises 34, 44, and 46.

STOP & THINK

You can put the calculated equilibrium concentrations into the expression for Q to check to see that $Q = K_c$ (within rounding error), as was shown at the end of Example 17-6.

Problem-Solving Tip Solving Quadratic Equations—Which Root Shall We Use?

Quadratic equations can be rearranged into standard form.

$$ax^2 + bx + c = 0$$

All can be solved by the quadratic formula, which is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (\text{Appendix A})$$

This formula gives *two* roots, both of which are *mathematically* correct. A foolproof way to determine which root of the equation has physical meaning is to substitute the value of the variable into the expressions for the equilibrium concentrations. For the extraneous root, one or more of these substitutions will lead to a negative concentration, which is physically impossible (there cannot be *less than none* of a substance present!). The correct root will give all positive concentrations. In Example 17-7, substitution of the extraneous root $x = 0.309$ would give $[A] = (0.300 - 0.309) M = -0.009 M$ and $[B] = (0.100 - 0.309) M = -0.209 M$. Either of these concentration values would be impossible, so we would know that 0.309 is an extraneous root. You should apply this test to subsequent calculations that involve solving a quadratic equation.

The following table summarizes Examples 17-6 and 17-7.

	Initial Concentrations (M)				Equilibrium Concentrations (M)			
	[A]	[B]	[C]	[D]	[A]	[B]	[C]	[D]
Example 17-6	0.200	0.200	0	0	0.025	0.025	0.175	0.175
Example 17-7	0.300	0.100	0	0	0.201	0.001	0.099	0.099

The data from the table can be substituted into the reaction quotient expression, Q , as a check (see margin). Even though the reaction is initiated by different relative amounts of reactants in the two cases, the ratios of equilibrium concentrations of products to reactants (each raised to the first power) agree within roundoff error.

► Check Example 17-6:

$$Q = \frac{[C][D]}{[A][B]} = \frac{(0.175)(0.175)}{(0.025)(0.025)}$$

$$Q = 49 = K_c$$

Check Example 17-7:

$$Q = \frac{(0.099)(0.099)}{(0.201)(0.001)}$$

$$Q = 49 = K_c$$

17-6 Disturbing a System at Equilibrium: Predictions

Once a reacting system has reached equilibrium, it remains at equilibrium until it is disturbed by some change of conditions. The guiding principle is known as **LeChatelier's Principle** (see Section 13-6).

► *LeChatelier* is pronounced "le-SHOT-lee-ay."

Unless otherwise noted, all content on this page is © Cengage Learning.

► Remember that the *value* of an equilibrium constant changes only with temperature.

► For reactions involving gases at constant temperature, changes in volume cause changes in pressure, and vice versa.

If a system at equilibrium is disturbed by changing its conditions (applying a stress), the system shifts in the direction that reduces the stress. Given sufficient time, a new state of equilibrium is established.

The reaction quotient, Q , helps us predict the direction of this shift. Three types of changes can disturb the equilibrium of a reaction.

1. Changes in concentration
2. Changes in pressure or volume (for reactions that involve gases)
3. Changes in temperature

We now study the effects of these types of stresses from a qualitative, or descriptive, point of view. In Section 17-8 we expand our discussion with quantitative examples.

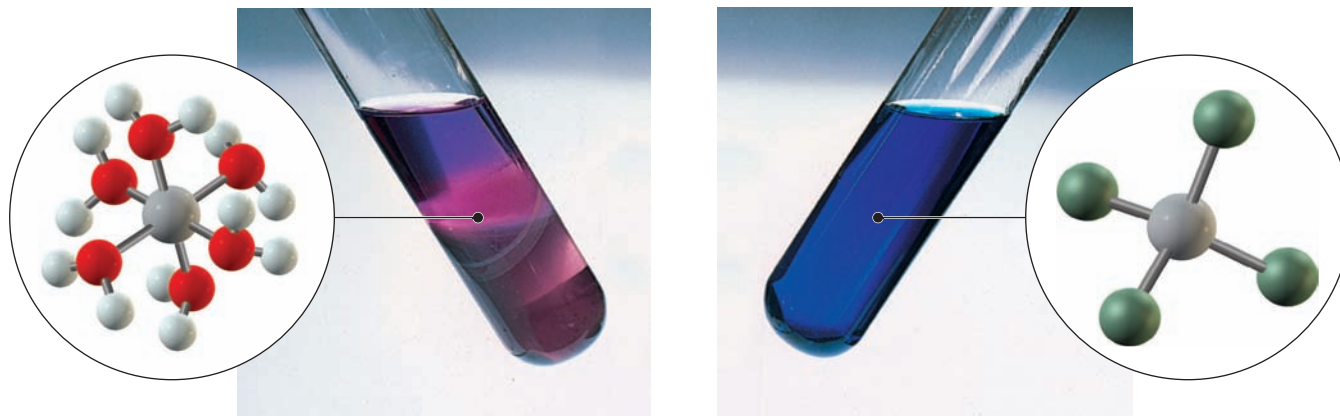
Changes in Concentration

Consider the following system *starting at equilibrium*.



When more of any reactant or product is *added* to the system, the value of Q changes so that it no longer matches K_c and the reaction is no longer at equilibrium. The stress due to the added substance is relieved by shifting the equilibrium in the direction that consumes some of the added substance, moving the value of Q back toward K_c . Let us compare the mass action expressions for Q and K_c . If more A or B is added, then $Q < K_c$, and the forward reaction occurs more rapidly and to a greater extent than the reverse reaction until equilibrium is reestablished. If more C or D is added, $Q > K_c$, and the reverse reaction occurs more rapidly and to a greater extent until equilibrium is reestablished.

Adding or removing reactants or products changes the value of Q . It *does not change* the value of K_c . Equilibrium is then reestablished by the reaction proceeding so as to change the value of Q back to the unaltered K_c value.



Effects of changes in concentration on the equilibrium



A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in isopropyl alcohol and water is purple (not shown) due to the mixture of $[\text{Co}(\text{OH})_6]^{2+}$ (pink) and $[\text{CoCl}_4]^{2-}$ (blue). When we add concentrated HCl , the excess Cl^- shifts the reaction to the right (blue, right photo). Adding $\text{AgNO}_3(\text{aq})$ removes some Cl^- by precipitation of $\text{AgCl}(\text{s})$ and favors the reaction to the left (produces more $[\text{Co}(\text{OH})_6]^{2+}$); the resulting solution is pink (left photo). Each model shows the structure of the cobalt complex species present in higher concentration; other ions and solvent molecules are not shown.

We can also view LeChatelier's Principle in the kinetic terms we used to introduce equilibrium. The rate of the forward reaction is proportional to the reactant concentrations raised to some powers:

$$\text{rate}_f = k_f[A]^x[B]^y$$

When we add more A to an equilibrium mixture, this rate increases so that it no longer matches the rate of the reverse reaction. As the reaction proceeds to the right, consuming some A and B and forming more C and D, the forward rate diminishes and the reverse rate increases until they are again equal. At that point, a new equilibrium condition has been reached, with more C and D than were present in the *original* equilibrium mixture. Not all of the added A has been consumed when the new equilibrium is reached, however.

If a reactant or product is *removed* from a system at equilibrium, the reaction that produces *that* substance occurs to a greater extent than its reverse. If some C or D is removed, then $Q < K$, and the forward reaction is favored until equilibrium is reestablished. If some A or B is removed, the reverse reaction is favored.

► The terminology used here is not as precise as we might like, but it is widely used. When we say that the equilibrium is "shifted to the left," we mean that the reaction to the left occurs to a greater extent than the reaction to the right.

Stress	Q	Direction of Shift of $A + B \rightleftharpoons C + D$
Increase concentration of A or B	$Q < K$	$\longrightarrow$ right
Increase concentration of C or D	$Q > K$	left $\longleftarrow$
Decrease concentration of A or B	$Q > K$	left $\longleftarrow$
Decrease concentration of C or D	$Q < K$	$\longrightarrow$ right

STOP & THINK

This tabulation summarizes a lot of useful information. Study it carefully.

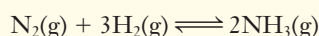
When a new equilibrium condition is established, (1) the rates of the forward and reverse reactions are again equal, and (2) K_c is again satisfied by the new concentrations of reactants and products.

Practical applications of changes of this type are of great economic importance. Removing a product of a reversible reaction forces the reaction to produce more product than could be obtained if the reaction were simply allowed to reach equilibrium.

EXAMPLE 17-8 Disturbing a System at Equilibrium: Predictions

Given the following reaction at equilibrium in a closed container at 500°C, predict the effect of each of the following changes on the amount of NH_3 present at equilibrium:

(a) forcing more H_2 into the system; (b) removing some NH_3 from the system.



Plan

We apply LeChatelier's Principle to each part of the question. We can reach the same conclusions by comparing Q with K , even though we don't have numerical values.

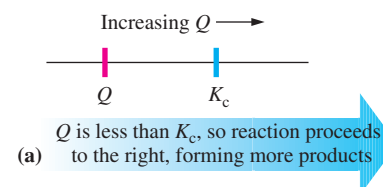
Solution

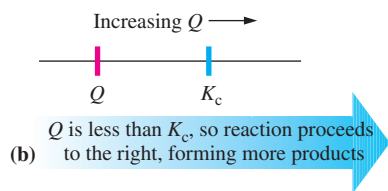
- (a) LeChatelier's Principle: Adding a substance favors the reaction that uses up that substance (forward in this case).

More NH_3 is formed.

Q vs. K_c : At the start, the reaction is at equilibrium, so $Q = K_c$. Then we add more H_2 , which *increases* $[\text{H}_2]$. Because $[\text{H}_2]$ is in the denominator of

$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$





this *decreases* the value of Q , making $Q < K_c$. To reestablish equilibrium, the reaction proceeds to the right.

More NH_3 is formed.

(b) LeChatelier's Principle: Removing a substance favors the reaction that produces that substance (forward in this case).

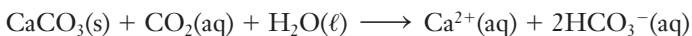
More NH_3 is formed.

Q vs. K_c : At the start, the reaction is at equilibrium, so $Q = K_c$. Then we remove some NH_3 , which *decreases* $[\text{NH}_3]$. Because $[\text{NH}_3]$ is in the numerator of Q , this *decreases* the value of Q , making $Q < K_c$. To reestablish equilibrium, the reaction proceeds to the right.

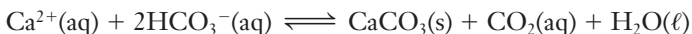
More NH_3 is formed.

At the new equilibrium, the concentration of any reactant or product that was added will still be greater than it was in the original equilibrium mixture. The concentration of any reactant or product that was removed will be less in the new equilibrium mixture because the reaction will have replaced only part of the removed material.

Another example of the shifting of equilibrium occurs in nature during the formation of stalactites and stalagmites in caves. Water containing carbon dioxide slowly passes through layers of limestone, CaCO_3 . The limestone dissolves according to the following reaction:



Equilibrium is established when the dissolved limestone reaches the limit of its solubility:



When the solution reaches a cave, carbon dioxide slowly escapes from the solution, and the subsequent shift in the equilibrium causes CaCO_3 to be precipitated. Deposits of CaCO_3 produce the attractive cave formations.

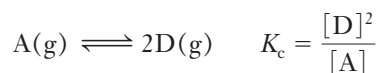
Changes in Volume and Pressure

Changes in pressure have little effect on the concentrations of solids or liquids because they are only slightly compressible. Changes in pressure do cause significant changes in concentrations of gases, however. Such changes therefore affect the value of Q for reactions in which the number of moles of gaseous reactants differs from the number of moles of gaseous products. For an ideal gas,

$$PV = nRT \quad \text{or} \quad P = \left(\frac{n}{V}\right)(RT)$$

The term (n/V) represents concentration, that is, mol/L. At constant temperature, n , R , and T are constants. Thus, if the volume occupied by a gas decreases, its partial pressure increases and its concentration (n/V) increases. If the volume of a gas increases, both its partial pressure and its concentration decrease.

Consider the following gaseous system at equilibrium.



At constant temperature, a decrease in volume (increase in pressure) increases the concentrations of both A and D. In the expression for Q , the concentration of D is squared and the concentration of A is raised to the first power. As a result, the numerator of Q increases more than the denominator as pressure increases. Thus, $Q > K_c$, and this equilibrium



Stalactites and stalagmites are formed by the precipitation of calcium carbonate, CaCO_3 , when gaseous CO_2 escapes from groundwater solutions.

shifts to the left. Conversely, an increase in volume (decrease in pressure) shifts this reaction to the right until equilibrium is reestablished, because $Q < K_c$. We can summarize the effect of pressure (volume) changes on *this* gas-phase system at equilibrium.

Stress	Q^*	Direction of Shift of $A(g) \rightleftharpoons 2D(g)$
Volume decrease, pressure increase	$Q > K_c$	Toward smaller number of moles of gas (left for <i>this</i> reaction)
Volume increase, pressure decrease	$Q < K_c$	Toward larger number of moles of gas (right for <i>this</i> reaction)

*In Q for *this* reaction, there are more moles of gaseous product than gaseous reactant.

In general, for reactions that involve gaseous reactants or products, LeChatelier's Principle allows us to predict the following results.

1. If there is *no change in the total number of moles of gases in the balanced chemical equation*, a volume (pressure) change does not affect the position of equilibrium; Q is unchanged by the volume (or pressure) change.
2. If a *balanced chemical equation involves a change in the total number of moles of gases*, changing the volume (or pressure) of a reaction mixture changes the value of Q ; it *does not change* the value of K_c . For such a reaction:
 - (a) A decrease in volume (increase in pressure) shifts a reaction in the direction that produces the *smaller total number of moles of gas*, until Q again equals K_c .
 - (b) An increase in volume (decrease in pressure) shifts a reaction in the direction that produces the *larger total number of moles of gas*, until Q again equals K_c .

The foregoing argument applies only when pressure changes are due to volume changes. It *does not apply* if the total pressure of a gaseous system is raised by merely pumping in an inert gas, for example, He. If the gas that is introduced is not involved in the reaction, the *partial pressure* of each reacting gas remains constant, so the system remains at equilibrium.

STOP & THINK

Study this tabulation carefully. How would these conclusions change for a reaction in which there are more moles of gaseous reactants than moles of gaseous products?

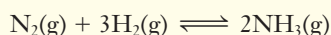
► One practical application of these ideas is illustrated in the next section by the Haber process.

STOP & THINK

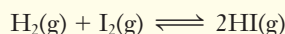
Many students do not realize that as a different gas is pumped into a container, the partial pressures of any gases already present do not change.

EXAMPLE 17-9 Disturbing a System at Equilibrium: Predictions

- (a) Given the following reaction at equilibrium in a closed container at 500°C, predict the effect of increasing the pressure by decreasing the volume.



- (b) Make the same prediction for the following reaction at high temperature.



Plan

We apply LeChatelier's Principle to predict the effect on each reaction.

Solution

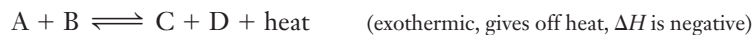
- (a) Increasing the pressure favors the reaction that produces the smaller number of moles of gas (forward in this case).

More NH_3 is formed.

- (b) This reaction involves the same number of moles of gas on both sides, so a pressure (volume) change does not disturb the equilibrium. There is **no effect on the position of equilibrium**.

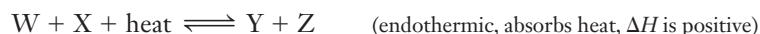
Changes in Temperature

Consider the following exothermic reaction at equilibrium:



Heat is produced by the forward (exothermic) reaction. Suppose we increase the temperature at constant pressure by adding heat to the system. This favors the reaction to the left, removing some of the extra heat. Lowering the temperature favors the reaction to the right as the system replaces some of the heat that was removed.

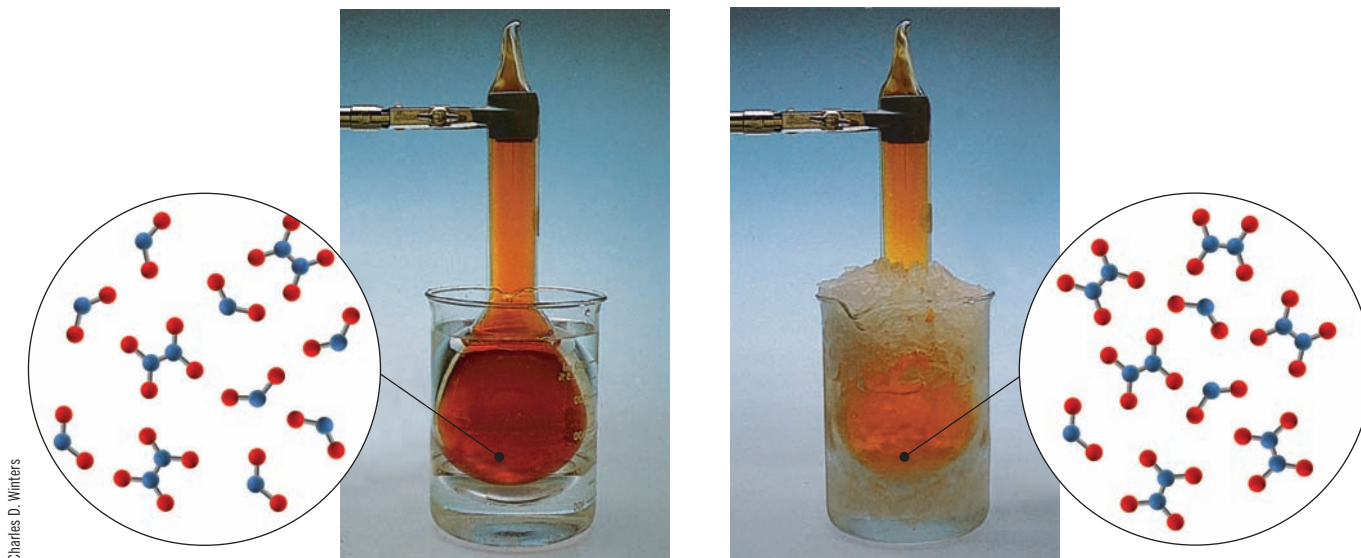
By contrast, for an endothermic reaction at equilibrium,



an increase in temperature at constant pressure favors the reaction to the right. A decrease in temperature favors the reaction to the left.

The *value of any equilibrium constant changes* as the temperature changes, as we will see in Section 17-13. Changing the temperature of a reaction at equilibrium thus causes Q to differ from K_c , but now this is because K_c has changed. The reaction then proceeds in the direction that moves Q toward the new value of K_c .

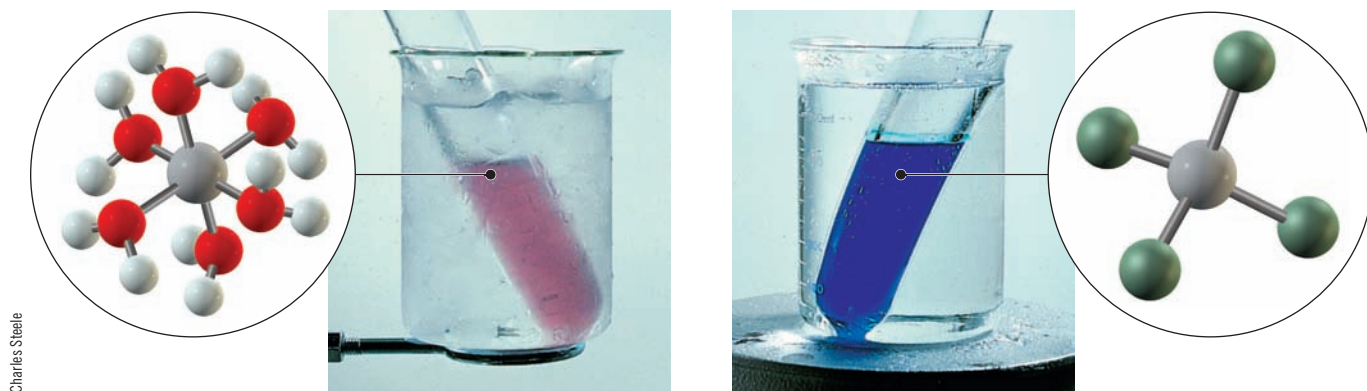
The K_c values of exothermic reactions decrease with increasing T .
 The K_c values of endothermic reactions increase with increasing T .
 No other stresses affect the value of K_c .



The gas-phase equilibrium for the *exothermic* reaction



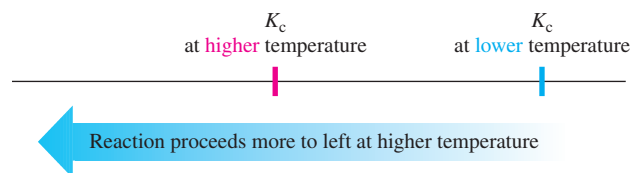
The two flasks contain the same *total mass* of gas. NO_2 is brown, whereas N_2O_4 is colorless. The higher temperature (50°C) of the flask on the left favors the reverse reaction; this mixture is more highly colored because it contains more NO_2 . The flask on the right, at the temperature of ice water, contains less brown NO_2 gas. The lower temperature favors the formation of the N_2O_4 . No matter how far the equilibrium shifts, both reactants and products will always be present.



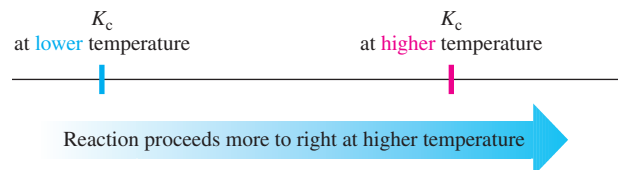
Charles Steele

Effect of temperature on the equilibrium of the *endothermic* reaction: $[\text{Co}(\text{OH}_2)_6]^{2+} + 4\text{Cl}^- + \text{heat} \rightleftharpoons [\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O}$
 We begin with a purple equilibrium mixture of the pink and blue complexes at room temperature (not shown). In hot water the forward reaction (endothermic) is favored and K_c is higher, so the solution is blue (right photo). At 0°C, the reverse reaction (exothermic) is favored and K_c is lower, so the solution is pink (left photo). Each model shows the structure of the cobalt complex species present in highest concentration; other ions and solvent molecules are not shown.

For an **exothermic** reaction



For an **endothermic** reaction



Addition of a Catalyst

Adding a catalyst to a system changes the rate of the reaction (see Section 16-9), but this *does not* shift the equilibrium in favor of either products or reactants. Because a catalyst affects the activation energy of *both* forward and reverse reactions equally, it changes both rate constants by the same factor, so their ratio, K_c , does not change.

Adding a catalyst to a reaction at equilibrium has no effect on the amounts of reactants or products; it changes neither Q nor K_c .

The same equilibrium mixture is achieved with or without the catalyst, but the equilibrium is established more quickly in the presence of a catalyst.

Not all reactions attain equilibrium; they may occur too slowly, or else products or reactants may be continually added or removed. Such is the case with most reactions in biological systems. On the other hand, some reactions, such as typical acid-base neutralizations, achieve equilibrium very rapidly.

STOP & THINK

Theoretically, in closed systems all chemical reactions are reversible and can be characterized with equilibrium constants. You may wonder if the equilibrium reactions described are somehow different from those used in previous chapters where only a single reaction arrow was used. Many of those reactions have large K values and proceed to make mainly products. Equilibrium concentrations (and double reaction arrows) are most meaningful for reactions that have K values that are neither extremely large nor extremely small and have observable quantities of both reactants and products at equilibrium.

► Can you use the Arrhenius equation (Section 16-8) to show that lowering the activation energy barrier increases forward and reverse rates by the same factor?

EXAMPLE 17-10 Disturbing a System at Equilibrium: Predictions

Given the following reaction at equilibrium in a closed container at 500°C, predict the effect of each of the following changes on the amount of NH_3 present at equilibrium: (a) raising the temperature; (b) lowering the temperature; (c) introducing some platinum catalyst. (d) How would the value of K_c change in each case?

**Plan**

We apply LeChatelier's Principle to each part of the question individually.

Solution

- (a) The negative value for ΔH tells us that the forward reaction is exothermic. Raising the temperature favors the endothermic reaction (reverse in this case).

Some NH_3 is used up.

- (b) Lowering the temperature favors the exothermic reaction (forward in this case).

More NH_3 is formed.

- (c) A catalyst does not favor either reaction.

It would have no effect on the amount of NH_3 .

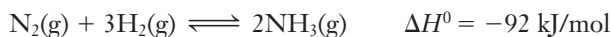
- (d) In (a), there is less product (NH_3) present at equilibrium at the higher temperature, so the value of K_c is smaller at the higher temperature. In (b), there is more product (NH_3) present at equilibrium at the lower temperature, so the value of K_c is greater at the lower temperature. In (c), the change (introduction of a catalyst) causes no change in equilibrium concentrations, so K_c does not change.

You should now work Exercises 54, 57, and 58.

► As Germany prepared for World War I, Britain controlled the seas and thus the access to the natural nitrates in India and Chile that were needed to prepare explosives. Fritz Haber (1868–1934) developed the process to provide a cheaper and more reliable source of explosives. Currently the process is used mainly to produce fertilizers. Large amounts of ammonia are converted into ammonium sulfate or ammonium nitrate for use as fertilizers. Approximately 100 pounds of NH_3 is used for this purpose per person in the United States each year.

17-7 The Haber Process: A Commercial Application of Equilibrium

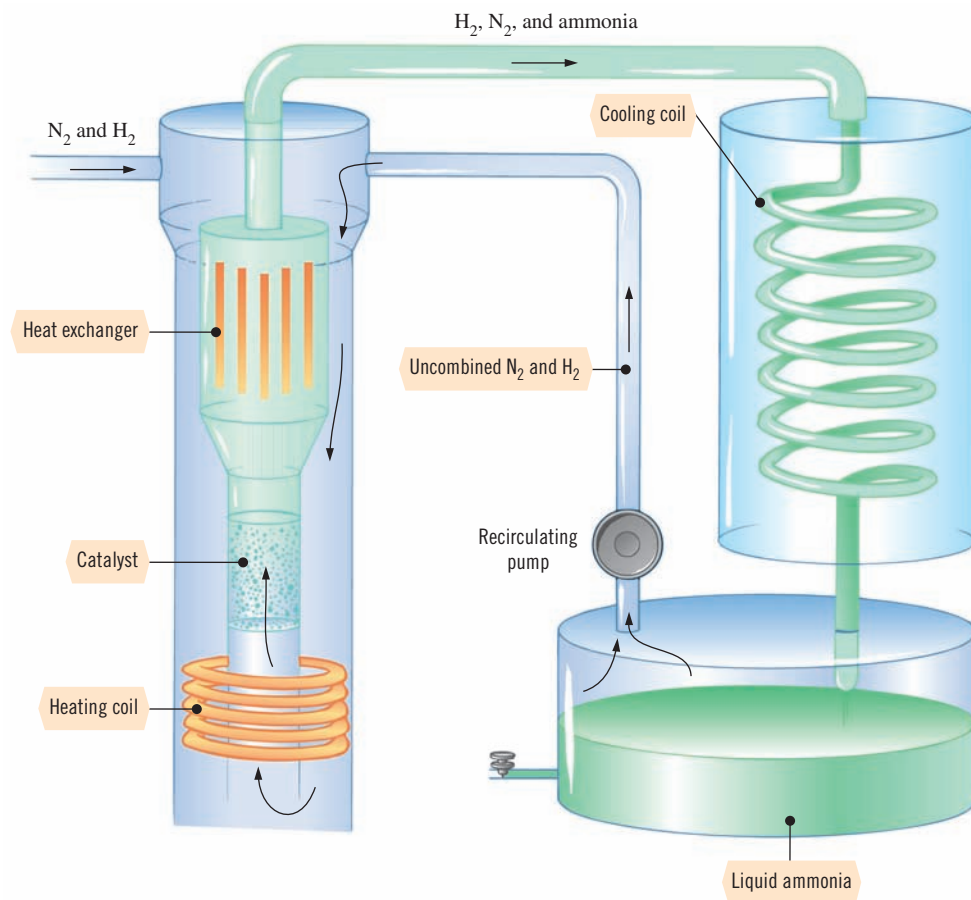
Nitrogen, N_2 , is very unreactive. The Haber process is the economically important industrial process by which atmospheric N_2 is converted to ammonia, NH_3 , a soluble, reactive compound. Innumerable dyes, plastics, explosives, fertilizers, and synthetic fibers are made from ammonia. The Haber process is an excellent practical application of LeChatelier Principle. It provides insight into kinetic and thermodynamic factors that influence reaction rates and the positions of equilibria. In this process the reaction between N_2 and H_2 to produce NH_3 is never allowed to reach equilibrium, but moves toward it.



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 3.6 \times 10^8 \quad (\text{at } 25^\circ\text{C})$$

The process is diagrammed in Figure 17-3. The reaction is carried out at about 450°C under pressures ranging from 200 to 1000 atmospheres. Hydrogen is obtained from coal gas or petroleum refining and nitrogen is obtained from liquefied air.

The value of K_c is 3.6×10^8 at 25°C. This very large value of K_c indicates that *if equilibrium were reached* at 25°C, virtually all of the N_2 and H_2 (mixed in a 1:3 mole ratio) would be converted into NH_3 . At 25°C, the reaction occurs so slowly, however, that no measurable amount of NH_3 is produced within a reasonable time. Thus, the large equilibrium constant (a thermodynamic factor) indicates that the reaction proceeds toward the right almost completely. It tells us *nothing*, however, about how fast the reaction occurs (a kinetic factor).



A nighttime photo of a large plant for the commercial production of ammonia, NH_3 . Such an installation can produce up to 7000 metric tons of ammonia per day. There are nearly 100 such plants in the world.

Figure 17-3 A simplified representation of the Haber process for synthesizing ammonia.

There are four moles of gas on the left side of the equation and only two moles of gas on the right, so increasing the pressure favors the production of NH_3 . The Haber process is therefore carried out at very high pressures, as high as the equipment will safely stand [see Example 17-9(a)].

The reaction is exothermic (ΔH_{rxn}^0 is negative), so decreasing the temperature favors the *formation* of NH_3 [see Example 17-10(b)]. But the rates of both forward and reverse reactions would decrease greatly as the temperature decreases.

The addition of a catalyst of finely divided iron and small amounts of selected oxides speeds up both the forward and reverse reactions. This allows NH_3 to be produced not only more rapidly but at a lower temperature, which increases the overall production of NH_3 and extends the life of the equipment.

Table 17-1 shows the effects of changes in temperature and pressure on the equilibrium yield of NH_3 , starting with 1:3 mole ratios of $\text{N}_2:\text{H}_2$. K_c changes by more than ten orders of magnitude, from 3.6×10^8 at 25°C to only 1.4×10^{-2} at 758°C . This tells us that the reaction proceeds *very far to the left* at high temperatures. Casual examination of the data might suggest that the reaction should be run at lower temperatures so that a higher

► In practice, the mixed reactants are compressed by special pumps and injected into the heated reaction vessel.

► Ten orders of magnitude is 10^{10} , that is,
 $1 \times 10^{10} = 10,000,000,000$

Table 17-1 Effect of T and P on Yield of Ammonia

$^\circ\text{C}$	K_c	Mole % NH_3 in Equilibrium Mixture		
		10 atm	100 atm	1000 atm
209	650	51	82	98
467	0.5	4	25	80
758	0.014	0.5	5	13

Unless otherwise noted, all content on this page is © Cengage Learning.



A major use of ammonia is as agricultural fertilizer.

percentage of the N_2 and H_2 would be converted into NH_3 . The reaction occurs so slowly, however, even in the presence of a catalyst, that it cannot be run economically at temperatures below about 450°C .

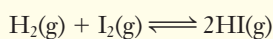
The emerging reaction mixture is cooled and NH_3 (bp = -33.43°C) is removed as a liquid. This prevents the reaction from reaching equilibrium and favors the forward reaction. The unreacted N_2 and H_2 are recycled. Excess N_2 is used to favor the reaction to the right.

17-8 Disturbing a System at Equilibrium: Calculations

We can use equilibrium constants to calculate new equilibrium concentrations that result from adding species to, or removing species from, a system at equilibrium.

EXAMPLE 17-11 Disturbing a System at Equilibrium: Calculations

Some hydrogen and iodine are mixed at 229°C in a 1.00-liter container. When equilibrium is established, the following concentrations are present: $[\text{HI}] = 0.490\text{ M}$, $[\text{H}_2] = 0.080\text{ M}$, and $[\text{I}_2] = 0.060\text{ M}$. If an additional 0.300 mol of HI is then added, what concentrations will be present when the new equilibrium is established?



Plan

We use the original equilibrium concentrations to calculate the value of K_c . Then we determine the new concentrations after some HI has been added and calculate Q . Comparing the value of Q to K_c tells us which reaction is favored. Then we can represent the new equilibrium concentrations. We substitute these representations into the K_c expression and solve for the new equilibrium concentrations.

Solution

Calculate the value of K_c from the first set of equilibrium concentrations.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.490)^2}{(0.080)(0.060)} = 50.$$

When we add 0.300 mol of HI to the 1.00-liter container, the $[\text{HI}]$ instantaneously increases by 0.300 M .

	$\text{H}_2(\text{g})$	$+$	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$
original equilibrium	0.080 M		0.060 M		0.490 M
mol/L added	0 M		0 M		+0.300 M
new initial conc'n	0.080 M		0.060 M		0.790 M

Substitution of these *new initial* concentrations into the reaction quotient gives

$$Q = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.790)^2}{(0.080)(0.060)} = 130$$

Because $Q > K_c$, the reaction proceeds to the left to establish a new equilibrium. The new equilibrium concentrations can be determined as follows. Let $x = \text{mol/L}$ of H_2 formed; so $x = \text{mol/L}$ of I_2 formed, and $2x = \text{mol/L}$ of HI consumed.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$
new initial conc'n	0.080 M		0.060 M		0.790 M
change due to rxn	$+x$ M		$+x$ M		$-2x$ M
new equilibrium	$(0.080 + x)$ M		$(0.060 + x)$ M		$(0.790 - 2x)$ M

Substitution of these values into K_c allows us to evaluate x .

$$K_c = 50. = \frac{(0.790 - 2x)^2}{(0.080 + x)(0.060 + x)} = \frac{0.624 - 3.16x + 4x^2}{0.0048 + 0.14x + x^2}$$

$$0.24 + 7.0x + 50x^2 = 0.624 - 3.16x + 4x^2$$

$$46x^2 + 10.2x - 0.38 = 0$$

Solution by the quadratic formula gives $x = 0.032$ and -0.25 .

Clearly, $x = -0.25$ is the extraneous root, because x cannot be less than zero in this case. This reaction does not consume a negative quantity of HI , because the reaction is proceeding toward the left. Thus, $x = 0.032$ is the root with physical meaning, so the new equilibrium concentrations are

$$[\text{H}_2] = (0.080 + x) \text{ M} = (0.080 + 0.032) \text{ M} = 0.112 \text{ M}$$

$$[\text{I}_2] = (0.060 + x) \text{ M} = (0.060 + 0.032) \text{ M} = 0.092 \text{ M}$$

$$[\text{HI}] = (0.790 - 2x) \text{ M} = (0.790 - 0.064) \text{ M} = 0.726 \text{ M}$$

In summary,

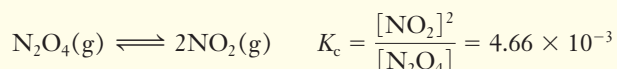
Original Equilibrium	Stress Applied	New Equilibrium
$[\text{H}_2] = 0.080 \text{ M}$ $[\text{I}_2] = 0.060 \text{ M}$ $[\text{HI}] = 0.490 \text{ M}$	Add 0.300 M HI	$[\text{H}_2] = 0.112 \text{ M}$ $[\text{I}_2] = 0.092 \text{ M}$ $[\text{HI}] = 0.726 \text{ M}$

You should now work Exercise 64.

We can also use the equilibrium constant to calculate new equilibrium concentrations that result from decreasing the volume (increasing the pressure) of a gaseous system that was initially at equilibrium.

EXAMPLE 17-12 Disturbing a System at Equilibrium: Calculations

At 22°C the equilibrium constant, K_c , for the following reaction is 4.66×10^{-3} . (a) If 0.800 mol of N_2O_4 were injected into a closed 1.00-liter container at 22°C , how many moles of each gas would be present at equilibrium? (b) If the volume were then halved (to 0.500 L) at constant temperature, how many moles of each gas would be present after the new equilibrium has been established?



► It is obvious that adding some HI favors the reaction to the left. If more than one substance is added to the reaction mixture, it might not be obvious which reaction will be favored. Calculating Q always lets us make the decision.

STOP & THINK

Equal amounts of H_2 and I_2 must be formed by the *new progress* of the reaction.

► To “consume a negative quantity of HI ” would be to form HI . The value $x = -0.25$ would lead to $[\text{H}_2] = (0.080 + x)\text{M} = (0.080 - 0.25)\text{M} = -0.17 \text{ M}$. A negative concentration is impossible, so $x = -0.25$ is the extraneous root.

STOP & THINK

We see that some of the additional HI is consumed, but not all of it. More HI remains after the new equilibrium is established than was present before the stress was imposed. The new equilibrium $[\text{H}_2]$ and $[\text{I}_2]$ are substantially greater than the original equilibrium concentrations, however.

Plan

(a) We are given the value of K_c and the initial concentration of N_2O_4 . We write the reaction summary, which gives the representation of the equilibrium concentrations. Then we substitute these into the K_c expression and solve for the new equilibrium concentrations.
 (b) We obtain the *new initial* concentrations by adjusting the equilibrium concentrations from Part (a) for the volume change. Then we solve for the *new* equilibrium concentrations as we did in Part (a).

Solution

(a) Let $x = \text{mol/L}$ of N_2O_4 consumed and $2x = \text{mol/L}$ of NO_2 formed.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
initial	0.800 M		0 M
change due to rxn	$-x M$		$+2x M$
equilibrium	$(0.800 - x) M$		$2x M$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 4.66 \times 10^{-3} = \frac{(2x)^2}{0.800 - x} = \frac{4x^2}{0.800 - x}$$

$$3.73 \times 10^{-3} - 4.66 \times 10^{-3}x = 4x^2$$

$$4x^2 + 4.66 \times 10^{-3}x - 3.73 \times 10^{-3} = 0$$

Solving by the quadratic formula gives $x = 3.00 \times 10^{-2}$ and $x = -3.11 \times 10^{-2}$. We use $x = 3.00 \times 10^{-2}$.

The original equilibrium concentrations are

$$[NO_2] = 2x M = 6.00 \times 10^{-2} M$$

$$[N_2O_4] = (0.800 - x) M = (0.800 - 3.00 \times 10^{-2}) M = 0.770 M$$

$$\underline{\quad} \text{ mol } NO_2 = 1.00 \text{ L} \times \frac{6.00 \times 10^{-2} \text{ mol } NO_2}{L} = 6.00 \times 10^{-2} \text{ mol } NO_2$$

$$\underline{\quad} \text{ mol } N_2O_4 = 1.00 \text{ L} \times \frac{0.770 \text{ mol } N_2O_4}{L} = 0.770 \text{ mol } N_2O_4$$

► The value of x is the number of moles per liter of N_2O_4 that react. So x must be positive and cannot be greater than 0.800 M.

$$0 < x < 0.800 M$$

► LeChatelier's Principle tells us that a decrease in volume (increase in pressure) favors the production of N_2O_4 . As before, we can confirm this by comparing Q with K_c .

$$Q = \frac{(0.120)^2}{1.54} = 9.35 \times 10^{-3}$$

$$Q > K_c$$

$\therefore$ $\xleftarrow{\text{shift left}}$

► The root $x = 0.104$ would give a *negative* concentration for NO_2 , which is impossible.

(b) When the volume of the reaction vessel is halved, the concentrations are doubled, so the *new initial* concentrations of N_2O_4 and NO_2 are $2(0.770 M) = 1.54 M$ and $2(6.00 \times 10^{-2} M) = 0.120 M$, respectively.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
new initial	1.54 M		0.120 M
change due to rxn	$+x M$		$-2x M$
new equilibrium	$(1.54 + x) M$		$(0.120 - 2x) M$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 4.66 \times 10^{-3} = \frac{(0.120 - 2x)^2}{1.54 + x}$$

Rearranging into the standard form of a quadratic equation gives

$$x^2 - 0.121x + 1.81 \times 10^{-3} = 0$$

Solving as before gives $x = 0.104$ and $x = 0.017$.

The maximum value of x is 0.060 M, because $2x$ may not exceed the concentration of NO_2 that was present after the volume was halved. Thus, $x = 0.017 M$ is the root with physical significance. The new equilibrium concentrations in the 0.500-liter container are

$$[NO_2] = (0.120 - 2x) M = (0.120 - 0.034) M = 0.086 M$$

$$[N_2O_4] = (1.54 + x) M = (1.54 + 0.017) M = 1.56 M$$

$$\underline{\hspace{1cm}} \text{ mol NO}_2 = 0.500 \text{ L} \times \frac{0.086 \text{ mol NO}_2}{\text{L}} = 0.043 \text{ mol NO}_2$$

$$\underline{\hspace{1cm}} \text{ mol N}_2\text{O}_4 = 0.500 \text{ L} \times \frac{1.56 \text{ mol N}_2\text{O}_4}{\text{L}} = 0.780 \text{ mol N}_2\text{O}_4$$

In summary,

First Equilibrium	Stress	New Equilibrium
0.770 mol of N ₂ O ₄	Decrease volume from	0.780 mol of N ₂ O ₄
0.0600 mol of NO ₂	1.00 L to 0.500 L	0.043 mol of NO ₂

You should now work Exercise 66.

STOP & THINK

The concentrations [N₂O₄] and [NO₂] *both increase* because of the large decrease in volume. However, the *number of moles* of N₂O₄ increases, while the *number of moles* of NO₂ decreases. We predict this from LeChatelier's Principle.



Problem-Solving Tip There Are Several Ways to Solve Equilibrium Problems

When a stress is applied to a system originally at equilibrium, it is no longer at equilibrium. As we did in Example 17-12(b), we can apply the stress to the *old equilibrium values* and then treat these as the new “initial values.” Alternatively, we could adjust the *original concentration values* to reflect the stress, and then treat these as the new “initial values.” We could consider [N₂O₄]_{initial} in Example 17-12(b) as the *original* 0.800 mol of N₂O₄ from part (a) in the *new* volume, 0.500 L. That is, [N₂O₄]_{initial} = 0.800 mol/0.500 L = 1.60 M, with no NO₂ having yet been formed. [NO₂]_{initial} = 0 M. From that starting point, the reaction would proceed to the *right*.

17-9 Partial Pressures and the Equilibrium Constant

It is often more convenient to measure pressures rather than concentrations of gases. Solving the ideal gas equation, $PV = nRT$, for pressure gives

$$P = \frac{n}{V}(RT) \quad \text{or} \quad P = M(RT)$$

► $\left(\frac{n}{V}\right)$ is $\left(\frac{\text{no. mol}}{\text{L}}\right)$

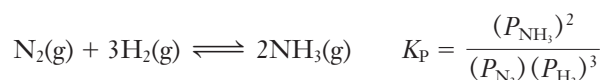
The pressure of a gas is directly proportional to its concentration (n/V). For reactions in which all substances that appear in the equilibrium constant expression are gases, we sometimes prefer to express the equilibrium constant in terms of partial pressures *in atmospheres* (K_P) rather than in terms of concentrations (K_C).

In general for a reaction involving gases,

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g) \quad K_P = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

► K_P has no units for the same reasons that K_C has no units.

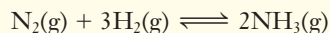
For instance, for the following reversible reaction,



Unless otherwise noted, all content on this page is © Cengage Learning.

EXAMPLE 17-13 Calculation of K_p

In an equilibrium mixture at 500°C, we find $P_{\text{NH}_3} = 0.147$ atm, $P_{\text{N}_2} = 6.00$ atm, and $P_{\text{H}_2} = 3.70$ atm. Evaluate K_p at 500°C for the following reaction.

**Plan**

We are given equilibrium partial pressures of all reactants and products. So we write the expression for K_p and substitute partial pressures in atmospheres into it.

Solution

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{(0.147)^2}{(6.00)(3.70)^3} = 7.11 \times 10^{-5}$$

You should now work Exercises 70 and 73.

STOP & THINK

One error that students sometimes make when solving K_p problems is to express pressures in torr. Remember that these pressures must be expressed in atmospheres.

17-10 Relationship Between K_p and K_c

If the ideal gas equation is rearranged, the molar concentration of a gas is

$$\left(\frac{n}{V}\right) = \frac{P}{RT} \quad \text{or} \quad M = \frac{P}{RT}$$

Substituting P/RT for n/V in the K_c expression for the $\text{N}_2\text{--H}_2\text{--NH}_3$ equilibrium gives the relationship between K_c and K_p for *this* reaction.

$$\begin{aligned} K_c &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{P_{\text{NH}_3}}{RT}\right)^2}{\left(\frac{P_{\text{N}_2}}{RT}\right)\left(\frac{P_{\text{H}_2}}{RT}\right)^3} = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} \times \frac{\left(\frac{1}{RT}\right)^2}{\left(\frac{1}{RT}\right)^4} \\ &= K_p(RT)^2 \quad \text{or} \quad K_p = K_c(RT)^{-2} \end{aligned}$$

In general the relationship between K_c and K_p is

$$K_p = K_c(RT)^{\Delta n} \quad \text{or} \quad K_c = K_p(RT)^{-\Delta n} \quad \Delta n = (n_{\text{gas prod}}) - (n_{\text{gas react}})$$

For reactions in which equal numbers of moles of gases appear on both sides of the equation, $\Delta n = 0$ and $K_p = K_c$.

In Example 17-1, we saw that for the ammonia reaction at 500°C (or 773 K), $K_c = 0.286$. We can describe this equilibrium in terms of partial pressures using K_p .

$$\begin{aligned} \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) &\rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta n = 2 - 4 = -2 \\ K_p &= K_c(RT)^{\Delta n} = (0.286)[(0.0821)(773)]^{-2} = 7.10 \times 10^{-5} \end{aligned}$$

This is essentially the same value we obtained in Example 17-13.

STOP & THINK

Δn refers to the numbers of moles of gaseous substances in the balanced equation, *not* in the reaction vessel.

Problem-Solving Tip Be Careful About the Value of R

To decide which value of R to use when you convert between K_c and K_p , you can reason as follows. K_c involves molar concentrations, for which the units are mol/L; K_p involves pressures expressed in atm. Thus the appropriate value of R to use for these conversions must include these units. We use $0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$, rounded to the number of places appropriate to the problem.

For *gas-phase reactions*, we can calculate the amounts of substances present at equilibrium using either K_p or K_c . The results are the same by either method (when they are both expressed in the same terms). To illustrate, let's solve the following problem by both methods.

EXAMPLE 17-14 Calculations with K_c and K_p

We place 10.0 grams of SbCl_5 in a 5.00-liter container at 448°C and allow the reaction to attain equilibrium. How many grams of SbCl_3 are present at equilibrium? Solve this problem (a) using K_c and molar concentrations, and (b) using K_p and partial pressures.



(a) Plan (using K_c)

We calculate the initial concentration of SbCl_5 , write the reaction summary, and represent the equilibrium concentrations; then we substitute into the K_c expression to obtain the equilibrium concentrations.

(a) Solution (using K_c)

Because we are given K_c , we use concentrations. The initial concentration of SbCl_5 is

$$[\text{SbCl}_5] = \frac{10.0 \text{ g SbCl}_5}{5.00 \text{ L}} \times \frac{1 \text{ mol}}{299 \text{ g}} = 0.00669 \text{ M SbCl}_5$$

Let $x = \text{mol/L}$ of SbCl_5 that react. In terms of molar concentrations, the reaction summary is

	SbCl_5	$\rightleftharpoons$	SbCl_3	+	Cl_2
initial	0.00669 M		0		0
change due to rxn	$-x \text{ M}$		$+x \text{ M}$		$+x \text{ M}$
equilibrium	$(0.00669 - x) \text{ M}$		$x \text{ M}$		$x \text{ M}$

$$K_c = \frac{[\text{SbCl}_3][\text{Cl}_2]}{[\text{SbCl}_5]}$$

$$2.51 \times 10^{-2} = \frac{(x)(x)}{0.00669 - x}$$

$$x^2 = 1.68 \times 10^{-4} - 2.51 \times 10^{-2}x$$

$$x^2 + 2.51 \times 10^{-2}x - 1.68 \times 10^{-4} = 0$$

Solving by the quadratic formula gives

$$x = 5.49 \times 10^{-3} \quad \text{and} \quad -3.06 \times 10^{-2} \text{ (extraneous root)}$$

$$[\text{SbCl}_3] = (0.00669 - x) \text{ M} = (0.00669 - 0.00549) \text{ M} = 1.20 \times 10^{-3} \text{ M}$$

$$\text{g SbCl}_3 = 5.00 \text{ L} \times \frac{1.20 \times 10^{-3} \text{ mol}}{\text{L}} \times \frac{299 \text{ g}}{\text{mol}} = 1.79 \text{ g SbCl}_3$$

Let us now solve the same problem *using K_p and partial pressures*.

(b) Plan (using K_p)

Calculate the initial partial pressure of SbCl_5 , and write the reaction summary. Substitution of the representations of the equilibrium partial pressures into K_p gives their values.

(b) Solution (using K_p)

We calculate the initial *pressure* of SbCl_5 in atmospheres, using $PV = nRT$.

$$P_{\text{SbCl}_5} = \frac{nRT}{V} = \frac{\left[(10.0 \text{ g}) \left(\frac{1 \text{ mol}}{299 \text{ g}} \right) \right] \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (721 \text{ K})}{5.00 \text{ L}} = 0.396 \text{ atm}$$

► The *partial pressure* of each substance is proportional to the *number of moles* of that substance.

► If we did not know the value of K_p , we could calculate it from the known value of K_c , using the relationship $K_p = K_c(RT)^{\Delta n}$.

► We see that within roundoff range the same result is obtained by both methods.

Clearly, $P_{\text{SbCl}_3} = 0$ and $P_{\text{Cl}_2} = 0$ because only SbCl_5 is present initially. We write the reaction summary in terms of partial pressures in atmospheres, because K_p refers to pressures in atmospheres.

Let y = decrease in pressure (atm) of SbCl_5 due to reaction. In terms of partial pressures, the reaction summary is

	SbCl_5	$\rightleftharpoons$	SbCl_3	+	Cl_2
initial	0.396 atm		0		0
change due to rxn	$-y$ atm		$+y$ atm		$+y$ atm
equilibrium	$(0.396 - y)$ atm		y atm		y atm

$$K_p = \frac{(P_{\text{SbCl}_3})(P_{\text{Cl}_2})}{P_{\text{SbCl}_5}} = 1.48 = \frac{(y)(y)}{0.396 - y}$$

$$0.586 - 1.48y = y^2 \quad y^2 + 1.48y - 0.586 = 0$$

Solving by the quadratic formula gives

$$y = 0.325 \text{ and } -1.80 \text{ (extraneous root)}$$

$$P_{\text{SbCl}_5} = (0.396 - y) = (0.396 - 0.325) = 0.071 \text{ atm}$$

We use the ideal gas law, $PV = nRT$, to calculate the number of moles of SbCl_5 .

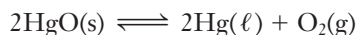
$$n = \frac{PV}{RT} = \frac{(0.071 \text{ atm})(5.00 \text{ L})}{\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(721 \text{ K})} = 0.0060 \text{ mol SbCl}_5$$

$$\underline{\quad} \text{ g SbCl}_5 = 0.0060 \text{ mol} \times \frac{299 \text{ g}}{\text{mol}} = \underline{1.8 \text{ g SbCl}_5}$$

You should now work Exercises 75 and 78.

17-11 Heterogeneous Equilibria

Thus far, we have considered only equilibria involving species in a single phase, that is, **homogeneous equilibria**. **Heterogeneous equilibria** involve species in more than one phase. Consider the following reversible reaction at 25°C.



A solid, a liquid, and a gas are all present when equilibrium is established for this system. Neither solids nor liquids are significantly affected by changes in pressure. The fundamental definition of the equilibrium constant in thermodynamics is in terms of the activities of the substances involved.

For any pure solid or pure liquid, the activity is taken as 1 (Section 17-2), so terms for pure liquids and pure solids *do not* appear in the K expressions for heterogeneous equilibria.

Thus, for the reaction

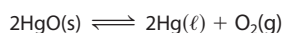


These equilibrium constant expressions indicate that equilibrium exists at a given temperature for *one and only one* concentration and one partial pressure of oxygen in contact with liquid mercury and solid mercury(II) oxide.



Charles Steele

► The decomposition reaction



The reaction is not at equilibrium here, because O_2 gas has been allowed to escape.

Unless otherwise noted, all content on this page is © Cengage Learning.

EXAMPLE 17-15 K_c and K_p for Heterogeneous Equilibrium

Write both K_c and K_p for the following reversible reactions.

- (a) $2\text{ZnS(s)} + 3\text{O}_2\text{(g)} \rightleftharpoons 2\text{ZnO(s)} + 2\text{SO}_2\text{(g)}$
 (b) $2\text{NH}_3\text{(g)} + \text{H}_2\text{SO}_4\text{(l)} \rightleftharpoons (\text{NH}_4)_2\text{SO}_4\text{(s)}$
 (c) $\text{S(s)} + \text{H}_2\text{SO}_3\text{(aq)} \rightleftharpoons \text{H}_2\text{S}_2\text{O}_3\text{(aq)}$

Plan

We apply the definitions of K_c and K_p to each reaction.

Solution

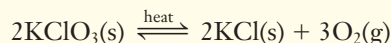
(a)	$K_c = \frac{[\text{SO}_2]^2}{[\text{O}_2]^3}$	$K_p = \frac{(P_{\text{SO}_2})^2}{(P_{\text{O}_2})^3}$
(b)	$K_c = \frac{1}{[\text{NH}_3]^2} = [\text{NH}_3]^{-2}$	$K_p = \frac{1}{(P_{\text{NH}_3})^2} = (P_{\text{NH}_3})^{-2}$
(c)	$K_c = \frac{[\text{H}_2\text{S}_2\text{O}_3]}{[\text{H}_2\text{SO}_3]}$	K_p undefined; no gases involved

STOP & THINK

Remember that concentrations or pressures for pure liquids and pure solids do not appear in the equilibrium constant expressions.

EXAMPLE 17-16 Heterogeneous Equilibria

The value of K_p is 27 for the thermal decomposition of potassium chlorate at a given high temperature. What is the partial pressure of oxygen in a closed container in which the following system is at equilibrium at the given temperature? (This can be a dangerous reaction.)

**Plan**

Because two solids, KClO_3 and KCl , and only one gas, O_2 , are involved, we see that K_p involves only the partial pressure of O_2 , that is, $K_p = (P_{\text{O}_2})^3$.

Solution

We are given

$$K_p = (P_{\text{O}_2})^3 = 27$$

Let $x \text{ atm} = P_{\text{O}_2}$ at equilibrium. Then we have

$$(P_{\text{O}_2})^3 = 27 = x^3 \quad x = 3.0 \text{ atm}$$

This tells us that the partial pressure of oxygen at equilibrium is 3.0 atm.

You should now work Exercises 80 and 91.

17-12 Relationship Between ΔG_{rxn}^0 and the Equilibrium Constant

Let's consider in thermodynamic terms what may happen when two substances are mixed together at constant temperature and pressure. First, as a result of mixing, there is usually an increase in entropy due to the increase in disorder. If the two substances can react with each other, the chemical reaction begins, heat is released or absorbed, and the concentrations of the substances in the mixture change. An additional change in entropy, which depends on changes in the nature of the reactants and products, also begins to occur. The evolution or absorption of heat energy, the changes in entropy, and the changes in concentrations all continue until equilibrium is established. Equilibrium may be reached with large amounts of products formed, with virtually all of the reactants remaining unchanged, or at *any* intermediate combination of concentrations.

Unless otherwise noted, all content on this page is © Cengage Learning.

► Thermodynamic standard states are (1) pure solids or pure liquids at 1 atm, (2) solutions of one-molar concentrations, and (3) gases at partial pressures of 1 atm.

The standard free energy change for a reaction is ΔG_{rxn}^0 . This is the free energy change that would accompany *complete* conversion of all reactants initially present at standard conditions to *all* products at standard conditions (see Section 15-16). The free energy change for any other concentrations or pressures is ΔG_{rxn} (no superscript zero). The two quantities are related by the equation

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^0 + RT \ln Q$$

R is the universal gas constant, T is the absolute temperature, and Q is the reaction quotient. When a system is *at equilibrium*, $\Delta G_{\text{rxn}} = 0$ (see Section 15-16) and $Q = K$. Recall that the reaction quotient may represent nonequilibrium concentrations (or partial pressures) of products and reactants. As reaction occurs, the free energy of the mixture and the concentrations change until at equilibrium $\Delta G_{\text{rxn}} = 0$, and the concentrations of reactants and products satisfy the equilibrium constant. At that point, Q becomes equal to K (see Section 17-4). Then

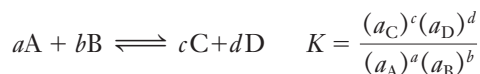
$$0 = \Delta G_{\text{rxn}}^0 + RT \ln K \quad (\text{at equilibrium})$$

Rearranging gives

$$\Delta G_{\text{rxn}}^0 = -RT \ln K$$

This equation shows the relationship between the standard free energy change and the *thermodynamic equilibrium constant*.

For the following generalized reaction, the **thermodynamic equilibrium constant** is defined in terms of the activities of the species involved.



where a_A is the activity of substance A, and so on (see Section 17-2). The mass action expression to which it is related involves concentration terms for species in solution and partial pressures for gases.

When the relationship $\Delta G_{\text{rxn}}^0 = -RT \ln K$ is used with

1. all gaseous reactants and products, K represents K_P ;
2. all solution reactants and products, K represents K_c ;
3. a mixture of solution and gaseous reactants, K represents the thermodynamic equilibrium constant, and we do not make the distinction between K_P and K_c .

Figure 17-4 displays the relationships between free energy and equilibrium. The *left* end of each curve represents the total free energy of the reactants and the *right* end of each curve represents the total free energy of the products at standard state conditions. The difference between them is ΔG_{rxn}^0 ; like K , ΔG_{rxn}^0 depends only on temperature and is a constant for any given reaction.

From the preceding equation that relates ΔG_{rxn}^0 and K , we see that when ΔG_{rxn}^0 is negative, $\ln K$ *must* be positive, and K is greater than 1. This tells us that products are favored over reactants at equilibrium. This case is illustrated in Figure 17-4a. When ΔG_{rxn}^0 is positive, $\ln K$ *must* be negative, and K is less than 1. This tells us that reactants are favored over products at equilibrium (Figure 17-4b). In the *rare* case of a chemical reaction for which $\Delta G_{\text{rxn}}^0 = 0$, then $K = 1$ and the numerator and the denominator must be equal in the equilibrium constant expression (i.e., $[C]^c [D]^d \dots = [A]^a [B]^b \dots$). These relationships are summarized as follows.

ΔG_{rxn}^0	K	Product Formation
$\Delta G_{\text{rxn}}^0 < 0$	$K > 1$	Products favored over reactants at equilibrium
$\Delta G_{\text{rxn}}^0 = 0$	$K = 1$	At equilibrium when $[C]^c [D]^d \dots = [A]^a [B]^b \dots$ (very rare)
$\Delta G_{\text{rxn}}^0 > 0$	$K < 1$	Reactants favored over products at equilibrium

STOP & THINK

The energy units of R must match those of ΔG^0 . We usually use

$$R = 8.314 \text{ J/mol} \cdot \text{K}$$

► We will encounter equilibrium calculations for solution and gaseous species in electrochemistry (see Chapter 21).

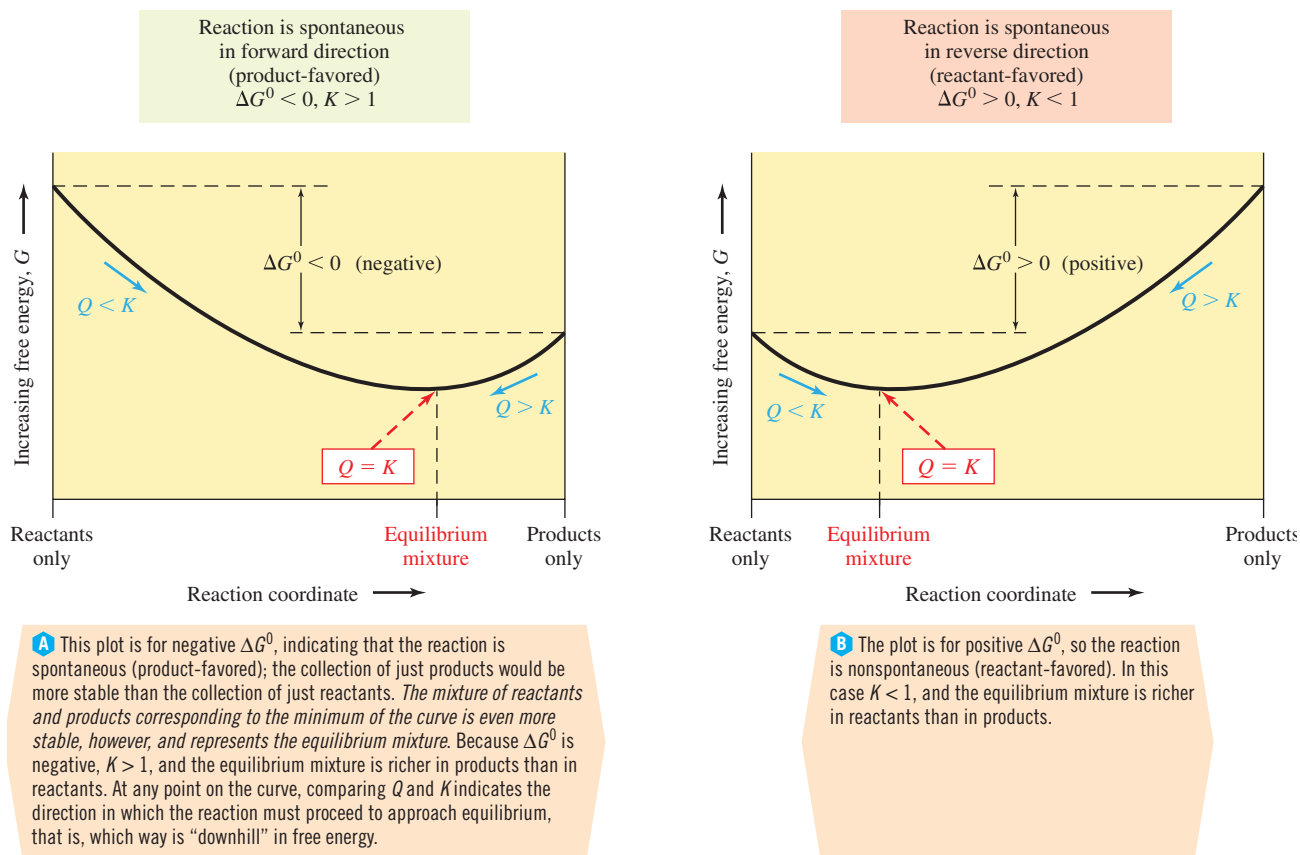


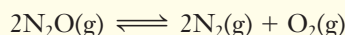
Figure 17-4 Variation in total free energy for a reversible reaction carried out at constant T . The standard free energy change, ΔG^0 , represents the free energy change for the complete conversion of reactants into products (both at standard state concentrations: 1 M or 1 atm).

The direction of approach to equilibrium and the actual free energy change (ΔG_{rxn}) are *not* constants. They vary with the conditions and the initial concentrations. If the initial concentrations correspond to $Q < K$, equilibrium is approached from left to right on the curves in Figure 17-4, and the forward reaction predominates. If $Q > K$, equilibrium is approached from right to left, and the reverse reaction predominates.

The magnitude of ΔG_{rxn}^0 indicates the *extent* to which a chemical reaction occurs under standard state conditions, that is, how far the reaction goes toward the formation of products before equilibrium is reached. The more negative the ΔG_{rxn}^0 value, the larger is the value of K and the more favorable is the formation of products. We think of some reactions as going “to completion.” These generally have *very negative* ΔG_{rxn}^0 values. The more positive the ΔG_{rxn}^0 value, the smaller is the value of K and the less favorable is the formation of products.

EXAMPLE 17-17 K Versus ΔG_{rxn}^0

Use the data in Appendix K to calculate K_P for the following reaction at 25°C.



Plan

The temperature is 25°C, so we evaluate ΔG_{rxn}^0 for the reaction from ΔG_f^0 values in Appendix K. The reaction involves only gases, so K is K_P . This means that $\Delta G_{\text{rxn}}^0 = -RT \ln K_P$. We solve for K_P .

STOP & THINK

Remember (Section 15-16) that if the temperature is *not* 25°C, you must calculate ΔG^0 for the reaction from the equation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

using tabulated values of ΔH_f^0 and S^0 as given in Appendix K. Review Examples 15-19 and 15-20.

► Units cancel when we express ΔG^0 in joules per mole. We interpret this as meaning “per mole of reaction”—that is, for the number of moles of each substance shown in the balanced equation.

► On some calculators, we evaluate e^x as follows: Enter the value of x , then press **INV** followed by **ln x**.

Solution

$$\begin{aligned}\Delta G_{\text{rxn}}^0 &= [2\Delta G_{\text{fN}_2(\text{g})}^0 + \Delta G_{\text{fO}_2(\text{g})}^0] - [2\Delta G_{\text{fN}_2\text{O}(\text{g})}^0] \\ &= [2(0) + 0] - [2(104.2)] = -208.4 \text{ kJ/mol, or } -2.084 \times 10^5 \text{ J/mol}\end{aligned}$$

This is a gas-phase reaction, so ΔG_{rxn}^0 is related to K_p by

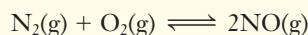
$$\begin{aligned}\Delta G_{\text{rxn}}^0 &= -RT \ln K_p \\ \ln K_p &= \frac{\Delta G_{\text{rxn}}^0}{-RT} = \frac{-2.084 \times 10^5 \text{ J/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = 84.1 \\ K_p &= e^{84.1} = 3.3 \times 10^{36}\end{aligned}$$

The very large value of K_p tells us that the equilibrium lies *very* far to the right. This reaction is so slow at 25°C, however, that very little N_2O decomposes to N_2 and O_2 at that temperature.

You should now work Exercise 84.

EXAMPLE 17-18 K Versus ΔG_{rxn}^0

In Examples 15-19 and 15-20 we evaluated ΔG_{rxn}^0 for the following reaction at 25°C and found it to be +173.1 kJ/mol. Calculate K_p at 25°C for this reaction.

**Plan**

In this example we use $\Delta G_{\text{rxn}}^0 = -RT \ln K_p$.

Solution

$$\begin{aligned}\Delta G_{\text{rxn}}^0 &= -RT \ln K_p \\ \ln K_p &= \frac{\Delta G_{\text{rxn}}^0}{-RT} = \frac{1.731 \times 10^5 \text{ J/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \\ &= -69.9 \\ K_p &= e^{-69.9} = 4.4 \times 10^{-31}\end{aligned}$$

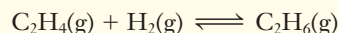
This very small number indicates that at equilibrium almost no N_2 and O_2 are converted to NO at 25°C. For all practical purposes, the reaction does not occur at 25°C.

You should now work Exercise 86.

A very important application of the relationships in this section is the use of measured K values to calculate ΔG_{rxn}^0 .

EXAMPLE 17-19 K Versus ΔG_{rxn}^0

The equilibrium constant, K_p , for the following reaction is 5.04×10^{17} at 25°C. Calculate ΔG_{298}^0 for the hydrogenation of ethylene to form ethane.

**Plan**

We use the relationship between ΔG^0 and K_p .

Solution

$$\begin{aligned}\Delta G_{298}^0 &= -RT \ln K_p \\ &= -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln(5.04 \times 10^{17}) \\ &= -1.01 \times 10^5 \text{ J/mol} \\ &= -101 \text{ kJ/mol}\end{aligned}$$

You should now work Exercise 88(a).

STOP & THINK

The energy units in ΔG , often given in kJ, must be converted to J to match those of R .

17-13 Evaluation of Equilibrium Constants at Different Temperatures

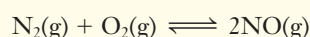
Chemists have determined equilibrium constants for thousands of reactions. It would be an impossibly huge task to catalog such constants for each reaction at every temperature of interest. Fortunately, there is no need to do this. If we determine the equilibrium constant, K_{T_1} , for a reaction at one temperature, T_1 , and also its ΔH° , we can then estimate the equilibrium constant at a second temperature, T_2 , using the **van't Hoff equation**.

$$\ln \left(\frac{K_{T_2}}{K_{T_1}} \right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Thus, if we know ΔH° for a reaction and K at a given temperature (say 298 K), we can use the van't Hoff equation to calculate the value of K at any other temperature.

EXAMPLE 17-20 Evaluation of K_p at Different Temperatures

We found in Example 17-18 that $K_p = 4.4 \times 10^{-31}$ at 25°C (298 K) for the following reaction. $\Delta H^\circ = 180.5$ kJ/mol for this reaction. Evaluate K_p at 2400. K.



Plan

We are given K_p at one temperature, 25°C, and the value of ΔH° . We are given the second temperature, 2400. K. These data allow us to evaluate the right side of the van't Hoff equation, which gives us $\ln(K_{T_2}/K_{T_1})$. Because we know K_{T_1} , we can find the value for K_{T_2} .

Solution

Let $T_1 = 298$ K and $T_2 = 2400$. K. Then

$$\ln \left(\frac{K_{T_2}}{K_{T_1}} \right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Let us first evaluate the right side of the equation.

$$\ln \left(\frac{K_{T_2}}{K_{T_1}} \right) = \frac{1.805 \times 10^5 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{298 \text{ K}} - \frac{1}{2400. \text{ K}} \right) = 63.8$$

Now take the inverse logarithm of both sides.

$$\frac{K_{T_2}}{K_{T_1}} = e^{63.8} = 5.1 \times 10^{27}$$

Solving for K_{T_2} and substituting the known value of K_{T_1} , we obtain

$$K_{T_2} = (5.1 \times 10^{27})(K_{T_1}) = (5.1 \times 10^{27})(4.4 \times 10^{-31}) = 2.2 \times 10^{-3} \text{ at } 2400. \text{ K}$$

You should now work Exercise 88(b–f).

► The van't Hoff equation assumes that ΔH° does not change with temperature. This is not strictly true, but the variation is generally quite small, so this equation gives good estimates of K_T .

► Compare the form of the van't Hoff equation to the Arrhenius equation (see Section 16-8) and to the Clausius–Clapeyron equation (see Section 13-9).

► 2400 K is a typical temperature inside the combustion chambers of automobile engines. Large quantities of N_2 and O_2 are present during gasoline combustion because the gasoline is mixed with air.

STOP & THINK

The positive value of ΔH° tells us that the reaction is endothermic. Thus, it is reasonable that the equilibrium constant is greater (2.2×10^{-3} compared to 4.4×10^{-31}) at the higher temperature of 2400. K.

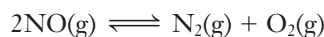


Problem-Solving Tip Use the Correct K

The K values that appear in the van't Hoff equation represent the *thermodynamic equilibrium constant* (see Section 17-12). For a gas-phase reaction (such as that in Example 17-20), K represents K_p ; if the value of K_c were given, we would have to convert it to K_p (see Section 17-10) before using the van't Hoff equation.

► The K_p value could be converted to K_c using the relationship $K_c = K_p(RT)^{-\Delta n}$ (see Section 17-10).

In Example 17-20 we see that K_T (K_p at 2400. K) is quite small, which tells us that the equilibrium favors N_2 and O_2 rather than NO . Nevertheless, K_T is very much larger than K_{T_1} , which is 4.4×10^{-31} . At 2400. K, significantly more NO is present at equilibrium relative to N_2 and O_2 than at 298 K. So automobiles emit small amounts of NO into the atmosphere that are sufficient to cause severe air pollution problems. Catalytic converters (see Section 16-9) are designed to catalyze the breakdown of NO into N_2 and O_2 .



This reaction is spontaneous. Catalysts do not shift the position of equilibrium. They favor neither consumption nor production of NO . They merely allow the system to reach equilibrium more rapidly. The time factor is very important because the NO stays in the automobile exhaust system for only a very short time.

KEY TERMS

Activity (of a component of an ideal mixture) A dimensionless quantity whose magnitude is equal to molar concentration in an ideal solution, equal to partial pressure (in atmospheres) in an ideal gas mixture, and defined as 1 for pure solids or liquids.

Chemical equilibrium A state of dynamic balance in which the rates of forward and reverse reactions are equal; there is no net change in concentrations of reactants or products while a system is at equilibrium.

Dynamic equilibrium An equilibrium in which processes occur continuously, with no *net* change.

Equilibrium constant (K) A dimensionless quantity that indicates the extent to which a reversible reaction occurs. K varies with temperature.

Heterogeneous equilibria Equilibria involving species in more than one phase.

Homogeneous equilibria Equilibria involving only species in a single phase, that is, all gases, all liquids, or all solids.

K_c Equilibrium constant with amounts of reactants and products expressed as molar concentrations.

K_p Equilibrium constant with amounts of reactants and products expressed as partial pressures.

LeChatelier's Principle If a stress (change of conditions) is applied to a system at equilibrium, the system shifts in the direction that reduces the stress, to move toward a new state of equilibrium.

Mass action expression For a reversible reaction,



the product of the molar concentrations of the products (species on the right), each raised to the power that corresponds to its coefficient in the balanced chemical equation, divided by the product of the concentrations of the reactants (species on the left), each raised to the power that corresponds to its coefficient in the balanced chemical equation. At equilibrium the mass action expression is equal to K ; at other conditions, it is Q .

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = Q \text{ or, at equilibrium, } K_c$$

Reaction quotient (Q) The mass action expression under any set of conditions (not necessarily equilibrium); its magnitude relative to K determines the direction in which reaction must occur to establish equilibrium.

Reversible reactions Reactions that do not go to completion and occur in both the forward and reverse directions.

Thermodynamic equilibrium constant The equilibrium constant defined in terms of activities of the products and reactants.

van't Hoff equation The relationship between ΔH° for a reaction and its equilibrium constants at two different temperatures.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Basic Concepts

1. ● Define and illustrate the following terms: (a) reversible reaction; (b) static equilibrium; (c) equilibrium constant.
2. Equilibrium constants do not have units. Explain.

3. ● Distinguish between the terms *static equilibrium* and *dynamic equilibrium*. Which kind does a chemical equilibrium represent?
4. ● (a) Describe three examples of static equilibrium. (b) Describe three examples of dynamic equilibrium (besides chemical equilibrium).

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

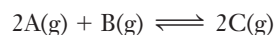
Unless otherwise noted, all content on this page is © Cengage Learning.

5. Explain the significance of (a) a very large value of K , (b) a very small value of K , and (c) a value of K of about 1.
6. What can be said about the magnitude of the equilibrium constant in a reaction whose equilibrium lies far to the right? to the left?
7. What is the relationship between equilibrium and the rates of opposing processes?
8. What does the value of an equilibrium constant tell us about the time required for the reaction to reach equilibrium?
9. When giving the value of an equilibrium constant, it is necessary also to write the balanced chemical equation. Why? Give examples to illustrate your explanation.
10. (a) How is the equilibrium constant related to the forward and reverse rate constants? (b) Can the rate expressions for forward and reverse reactions be written from the balanced chemical equation? Explain. (c) Can the equilibrium constant expression be written from the balanced chemical equation? Explain.
11. (a) Sketch a set of curves similar to those in Figure 17-2 for concentration changes over time for a reaction



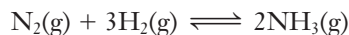
assuming that K is much greater than 1. In each case, assume that A and B start at the same concentration and that no C or D are present. (b) Repeat part (a) for the case that K is much less than 1.

12. (a) Sketch a set of curves similar to those in Figure 17-2 for concentration changes over time for a reaction



assuming that K is much greater than 1. In each case, assume that A and B start at the same concentration and that no C is present. (b) Repeat part (a) for the case that K is much less than 1.

13. At some temperature, the reaction



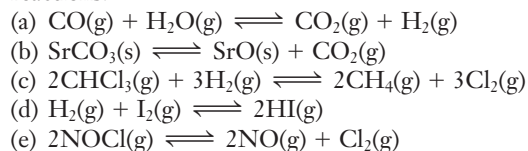
has an equilibrium constant K_c numerically equal to 1. State whether each of the following is true or false, and explain why. (a) An equilibrium mixture must have the H_2 concentration three times that of N_2 and the NH_3 concentration twice that of H_2 . (b) An equilibrium mixture must have the H_2 concentration three times that of N_2 . (c) A mixture in which the H_2 concentration is three times that of N_2 and the NH_3 concentration is twice that of N_2 could be an equilibrium mixture. (d) A mixture in which the concentration of each reactant and each product is 1 M is an equilibrium mixture. (e) Any mixture in which the concentrations of all reactants and products are equal is an equilibrium mixture. (f) An equilibrium mixture must have equal concentrations of all reactants and products.

14. Why do we omit concentrations of pure solids and pure liquids from equilibrium constant expressions?
15. Consider the following compounds, in the states indicated, as possible reactants or products in a chemical reaction. Which of these compounds would be omitted from the equilibrium constant expression? Explain. $H_2O(s)$, $H_2O(l)$, $H_2O(g)$, $HCl(g)$, $HCl(aq)$, $NaHCO_3(s)$, $CH_3OH(l)$, $CH_3OH(aq)$, $Cl_2(aq)$, $N_2(g)$, $NH_3(l)$, $CO(g)$, and $Fe_2O_3(s)$.

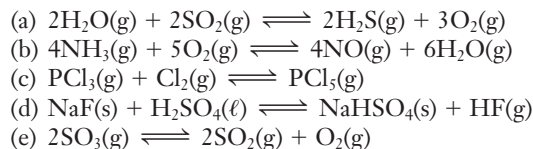
16. Consider the following compounds, in the states indicated, as possible reactants or products in a chemical reaction. Which of these compounds would be omitted from the equilibrium constant expression? Explain. $CaCO_3(s)$, $H_2SO_4(l)$, $NaOH(s)$, $NaOH(aq)$, $O_2(g)$, $CH_3COOH(l)$, $CH_3COOH(aq)$, $HI(g)$, $I_2(s)$, $C(\text{graphite})$, and $SO_3(g)$.

Equilibrium Constant Expression and Value of K

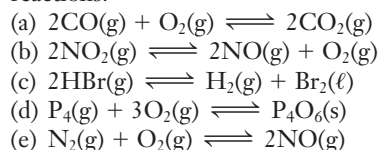
17. Write the expression for K_c for each of the following reactions:



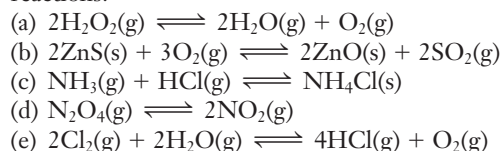
18. Write the expression for K_c for each of the following reactions:



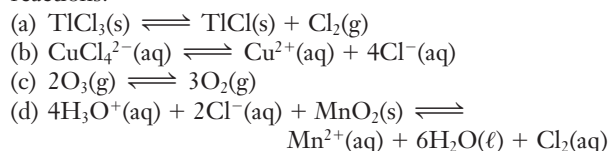
19. Write the expression for K_c for each of the following reactions:



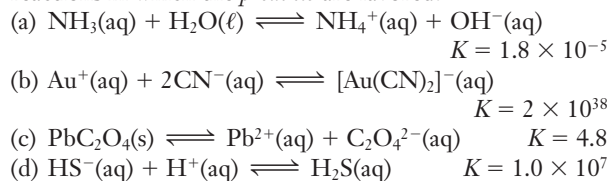
20. Write the expression for K_c for each of the following reactions:



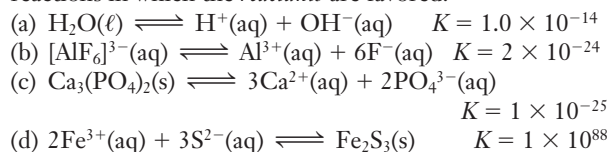
21. Write the expression for K_c for each of the following reactions:



22. On the basis of the equilibrium constant values, choose the reactions in which the *products* are favored.

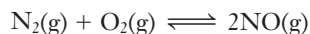


23. On the basis of the equilibrium constant values, choose the reactions in which the *reactants* are favored.



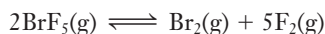
Calculation of K

24. The reaction between nitrogen and oxygen to form NO(g) is represented by the chemical equation



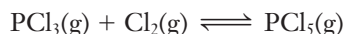
Equilibrium concentrations of the gases at 1500 K are 6.4×10^{-3} mol/L for N_2 , 1.7×10^{-3} mol/L for O_2 , and 1.1×10^{-5} mol/L for NO . Calculate the value of K_c at 1500 K from these data.

25. At elevated temperatures, BrF_5 establishes the following equilibrium.



The equilibrium concentrations of the gases at 1500 K are 0.0064 mol/L for BrF_5 , 0.0018 mol/L for Br_2 , and 0.0090 mol/L for F_2 . Calculate the value of K_c .

26. At some temperature the reaction



is at equilibrium when the concentrations of PCl_3 , Cl_2 , and PCl_5 are 10.0, 9.0, and 12.0 mol/L, respectively. Calculate the value of K_c for this reaction at that temperature.

27. For the reaction



the value of the equilibrium constant, K_c , is 1.845 at a given temperature. We place 0.500 mole CO and 0.500 mole H_2O in a 1.00-L container at this temperature and allow the reaction to reach equilibrium. What will be the equilibrium concentrations of all substances present?

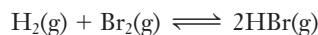
28. Given: $\text{A(g)} + \text{B(g)} \rightleftharpoons \text{C(g)} + 2\text{D(g)}$
One mole of A and one mole of B are placed in a 0.400-liter container. After equilibrium has been established, 0.20 mole of C is present in the container. Calculate the equilibrium constant, K_c , for the reaction.

29. The reaction



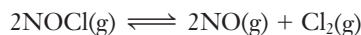
has an equilibrium constant, K_c , of 170 at 25°C . If 2.0×10^{-3} mol of NO_2 is present in a 10.-L flask along with 1.5×10^{-3} mol of N_2O_4 , is the system at equilibrium? If it is not at equilibrium, does the concentration of NO_2 increase or decrease as the system proceeds to equilibrium?

30. For the following equation, $K_c = 7.9 \times 10^{11}$ at 500. K.



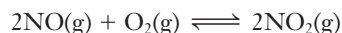
- (a) $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Br}_2(\text{g}) \rightleftharpoons \text{HBr}(\text{g})$ $K_c = ?$
(b) $2\text{HBr}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{Br}_2(\text{g})$ $K_c = ?$
(c) $4\text{HBr}(\text{g}) \rightleftharpoons 2\text{H}_2(\text{g}) + 2\text{Br}_2(\text{g})$ $K_c = ?$

31. Nitrosyl chloride, NOCl , decomposes to NO and Cl_2 at high temperatures.



Suppose you place 2.00 mol NOCl in a 1.0-L flask and raise the temperature to 462°C . When equilibrium has been established, 0.66 mol NO is present. Calculate the equilibrium constant, K_c , for the decomposition reaction from these data.

32. An equilibrium mixture contains 3.00 mol CO , 2.00 mol Cl_2 , and 9.00 mol COCl_2 in a 50.-L reaction flask at 800. K. Calculate the value of the equilibrium constant, K_c , for the reaction $\text{CO(g)} + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})$ at this temperature.
33. NO and O_2 are mixed in a container of fixed volume kept at 1000 K. Their initial concentrations are 0.0200 mol/L and 0.0300 mol/L, respectively. When the reaction



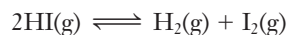
has come to equilibrium, the concentration of NO_2 is 2.2×10^{-3} mol/L. Calculate (a) the concentration of NO at equilibrium, (b) the concentration of O_2 at equilibrium, and (c) the equilibrium constant, K_c , for the reaction.

34. Antimony pentachloride decomposes in a gas-phase reaction at high temperatures.



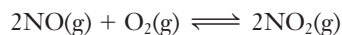
(a) At some temperature, an equilibrium mixture in a 5.00-L container is found to contain 6.91 g of SbCl_5 , 16.45 g of SbCl_3 , and 5.11 g of Cl_2 . Evaluate K_c . (b) If 25.0 grams of SbCl_5 is placed in the 5.00-L container and allowed to establish equilibrium at the temperature in part (a), what will be the equilibrium concentrations of all species?

35. At standard temperature and pressure, the reaction indicated by the following equation has an equilibrium constant, K_c , equal to 0.021.



Calculate the equilibrium constant, K_c , for the reverse equation.

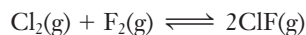
36. The following reaction has an equilibrium constant, K_c , equal to 1538 at $1800.^\circ\text{C}$.



Calculate the equilibrium constant, K_c , for the reverse equation.

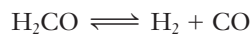
The Reaction Quotient, Q

37. Define the reaction quotient, Q . Distinguish between Q and K .
38. Why is it useful to compare Q with K ? What is the situation when (a) $Q = K$? (b) $Q < K$? (c) $Q > K$?
39. How does the form of the reaction quotient compare with that of the equilibrium constant? What is the difference between these two expressions?
40. If the reaction quotient is larger than the equilibrium constant, what will happen to the reaction? What will happen if $Q < K$?
41. $K_c = 19.9$ for the reaction



What will happen in a reaction mixture originally containing $[\text{Cl}_2] = 0.5$ mol/L, $[\text{F}_2] = 0.2$ mol/L, and $[\text{ClF}] = 7.3$ mol/L?

42. The concentration equilibrium constant for the gas-phase reaction



has the numerical value 0.50 at a given temperature. A mixture of H_2CO , H_2 , and CO is introduced into a flask at this temperature. After a short time, analysis of a small sample of the reaction mixture shows the concentrations to be $[\text{H}_2\text{CO}] = 0.50\text{ M}$, $[\text{H}_2] = 0.80\text{ M}$, and $[\text{CO}] = 0.25\text{ M}$. Classify each of the following statements about this reaction mixture as true or false.

- The reaction mixture is at equilibrium.
- The reaction mixture is not at equilibrium, but no further reaction will occur.
- The reaction mixture is not at equilibrium, but will move toward equilibrium by using up more H_2CO .
- The forward rate of this reaction is the same as the reverse rate.

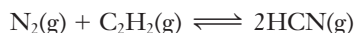
43. The value of K_c at 25°C for



is 3.7×10^{-23} . Describe what will happen if 3.5 mol of CO and 3.5 mol of CO_2 are mixed in a 1.5-L graphite container with a suitable catalyst to make the reaction “go” at this temperature.

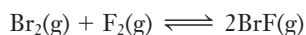
Uses of the Equilibrium Constant, K_c

44. For the reaction described by the equation



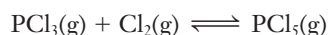
$K_c = 2.3 \times 10^{-4}$ at $300.^\circ\text{C}$. What is the equilibrium concentration of hydrogen cyanide if the initial concentrations of N_2 and acetylene (C_2H_2) were 3.5 mol/L and 2.5 mol/L, respectively?

45. The equilibrium constant, K_c , for the reaction



is 55.3. What are the equilibrium concentrations of all these gases if the initial concentrations of bromine and fluorine were both 0.240 mol/L?

46. $K_c = 96.2$ at 400. K for the reaction



What is the concentration of Cl_2 at equilibrium if the initial concentrations were 0.24 mol/L for PCl_3 and 5.5 mol/L for Cl_2 ?

47. $K_c = 5.85 \times 10^{-3}$ at 25°C for the reaction



Twenty-two (22.0) grams of N_2O_4 is confined in a 5.00-L flask at 25°C . Calculate (a) the number of moles of NO_2 present at equilibrium, and (b) the percentage of the original N_2O_4 that is dissociated.

48. The reaction of iron and water vapor results in an equilibrium



and an equilibrium constant, K_c , of 4.6 at $850.^\circ\text{C}$. What is the concentration of hydrogen present at equilibrium if the reaction is initiated with 24 g of H_2O and excess Fe in a 10.0-liter container?

49. The reaction of iron and water vapor results in an equilibrium



and an equilibrium constant, K_c , of 4.6 at $850.^\circ\text{C}$. What is the concentration of water present at equilibrium if the reaction is initiated with 7.5 g of H_2 and excess iron oxide, Fe_3O_4 , in a 15.0-liter container?

50. Carbon dioxide reacts with hot carbon in the form of graphite. The equilibrium constant, K_c , for the reaction is 10.0 at $850.^\circ\text{C}$.



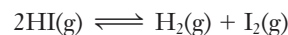
If 24.5 g of carbon monoxide is placed in a 2.50-L graphite container and heated to $850.^\circ\text{C}$, what is the mass of carbon dioxide at equilibrium?

51. Carbon dioxide reacts with hot carbon in the form of graphite. The equilibrium constant, K_c , for the reaction is 10.0 at $850.^\circ\text{C}$.



If 25.0 g of carbon dioxide and 55.0 g of graphite are placed in a 2.50-L reaction vessel and heated to $850.^\circ\text{C}$, what is the mass of carbon monoxide at equilibrium?

52. A 75.7-gram sample of HI was placed in a 1.50-L reaction vessel and allowed to come to equilibrium as illustrated in the following equation



The equilibrium constant, K_c , is 0.830. Calculate the concentration of each species present at equilibrium.

Factors That Influence Equilibrium

53. State LeChatelier's Principle. Which factors have an effect on a system at equilibrium? How does the presence of a catalyst affect a system at chemical equilibrium? Explain your answer.

54. What will be the effect of increasing the total pressure on the equilibrium conditions for (a) a chemical equation that has more moles of gaseous products than gaseous reactants, (b) a chemical equation that has more moles of gaseous reactants than gaseous products, (c) a chemical equation that has the same number of moles of gaseous reactants and gaseous products, and (d) a chemical equation in which all reactants and products are pure solids, pure liquids, or in an aqueous solution?

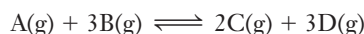
55. Suppose the following exothermic reaction is allowed to reach equilibrium.



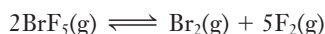
Then we make each of the following changes and allow the reaction to reestablish equilibrium. Tell whether the amount of B present at the new equilibrium will be (i) greater than, (ii) less than, or (iii) the same as the amount of B before the change was imposed.



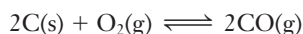
- (a) The temperature is decreased while the volume is kept constant;
 (b) more A is added;
 (c) more C is added;
 (d) a small amount of D is removed;
 (e) the pressure is increased by decreasing the volume.
56. Suppose the following exothermic reaction is allowed to reach equilibrium.



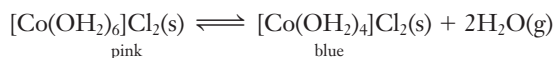
- Then we make each of the following changes and allow the reaction to reestablish equilibrium. For each change, tell whether the value of the equilibrium constant will be (i) greater than, (ii) less than, or (iii) the same as before the change was imposed.
- (a) The temperature is increased while the volume is kept constant;
 (b) more A is added;
 (c) more C is added;
 (d) a small amount of D is removed;
 (e) the pressure is decreased by increasing the volume.
57. What would be the effect on an equilibrium mixture of Br_2 , F_2 , and BrF_5 if the total pressure of the system were decreased?



58. What would be the effect on an equilibrium mixture of carbon, oxygen, and carbon monoxide if the total pressure of the system were decreased?



59. A weather indicator can be made with a hydrate of cobalt(II) chloride, which changes color as a result of the following reaction.

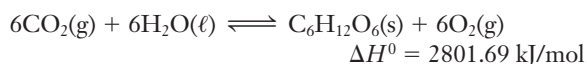


Does a pink color indicate “moist” or “dry” air? Explain.



Cobalt(II) chloride hexahydrate

60. Predict whether the equilibrium for the photosynthesis reaction described by the equation



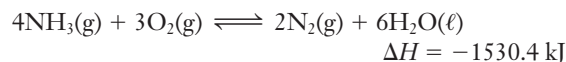
would (i) shift to the right, (ii) shift to the left, or (iii) remain unchanged if (a) $[\text{CO}_2]$ were decreased; (b) P_{O_2} were increased; (c) one half of the $\text{C}_6\text{H}_{12}\text{O}_6$ were removed; (d) the total pressure were decreased; (e) the temperature were increased; (f) a catalyst were added.

61. What would be the effect of increasing the temperature on each of the following systems at equilibrium?
- (a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI(g)} \quad \Delta H^\circ = -9.45 \text{ kJ/mol}$
 (b) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \quad \Delta H^\circ = 92.5 \text{ kJ/mol}$
 (c) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \quad \Delta H^\circ = -198 \text{ kJ/mol}$
 (d) $2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2(\text{g}) \quad \Delta H^\circ = 75 \text{ kJ/mol}$
 (e) $\text{C(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2(\text{g}) \quad \Delta H^\circ = 131 \text{ kJ/mol}$

62. What would be the effect of increasing the pressure by decreasing the volume on each of the following systems at equilibrium?

- (a) $2\text{CO(g)} + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$
 (b) $2\text{NO(g)} \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$
 (c) $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
 (d) $\text{Ni(s)} + 4\text{CO(g)} \rightleftharpoons \text{Ni(CO)}_4(\text{g})$
 (e) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

63. Consider the system



How will the amount of ammonia at equilibrium be affected by

- (a) removing $\text{O}_2(\text{g})$?
 (b) adding $\text{N}_2(\text{g})$?
 (c) adding water?
 (d) expanding the container at constant pressure?
 (e) increasing the temperature?

64. Given: $\text{A(g)} + \text{B(g)} \rightleftharpoons \text{C(g)} + \text{D(g)}$

- (a) At equilibrium a 1.00-liter container was found to contain 1.60 moles of C, 1.60 moles of D, 0.40 mole of A, and 0.40 mole of B. Calculate the equilibrium constant for this reaction.
 (b) If 0.20 mole of B and 0.20 mole of C are added to this system, what will the new equilibrium concentration of A be?

65. Given: $\text{A(g)} + \text{B(g)} \rightleftharpoons \text{C(g)} + \text{D(g)}$

When one mole of A and one mole of B are mixed and allowed to reach equilibrium at room temperature, the mixture is found to contain $\frac{2}{3}$ mole of C.

- (a) Calculate the equilibrium constant.
 (b) If two moles of A were mixed with two moles of B and allowed to reach equilibrium, how many moles of C would be present at equilibrium?

66. Given: $\text{A(g)} \rightleftharpoons \text{B(g)} + \text{C(g)}$

- (a) When the system is at equilibrium at $200.^\circ\text{C}$, the concentrations are found to be: $[\text{A}] = 0.30 \text{ M}$, $[\text{B}] = [\text{C}] = 0.25 \text{ M}$. Calculate K_c .
 (b) If the volume of the container in which the system is at equilibrium is suddenly doubled at $200.^\circ\text{C}$, what will be the new equilibrium concentrations?
 (c) Refer back to part (a). If the volume of the container is suddenly halved at $200.^\circ\text{C}$, what will be the new equilibrium concentrations?

67. The equilibrium constant, K_c , for the dissociation of phosphorus pentachloride is 9.3×10^{-2} at 252°C . How many moles and grams of PCl_5 must be added to a 2.0-liter flask to obtain a Cl_2 concentration of 0.17 M ?



68. At 25°C, K_c is 5.84×10^{-3} for the dissociation of dinitrogen tetroxide to nitrogen dioxide.



- Calculate the equilibrium concentrations of both gases when 4.00 grams of N_2O_4 is placed in a 2.00-liter flask at 25°C.
- What will be the new equilibrium concentrations if the volume of the system is suddenly increased to 3.00 liters at 25°C?
- What will be the new equilibrium concentrations if the volume is decreased to 1.00 liter at 25°C?

K in Terms of Partial Pressures

- Write the K_p expression for each reaction in Exercise 17.
- Under what conditions would K_c and K_p for a reaction be numerically equal? Are K_c and K_p numerically equal for any of the reactions in Exercises 17 and 18? Which ones?
- 0.0100 mol of NH_4Cl and 0.0100 mol of NH_3 are placed in a closed 2.00-L container and heated to 603 K. At this temperature, all the NH_4Cl vaporizes. When the reaction

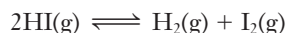


has come to equilibrium, 5.8×10^{-3} mol of HCl is present. Calculate (a) K_c and (b) K_p for this reaction at 603 K.

- CO_2 is passed over graphite at 500. K. The emerging gas stream contains 4.0×10^{-3} mol percent CO . The total pressure is 1.00 atm. Assume that equilibrium is attained. Find K_p for the reaction



- At 425°C, the equilibrium partial pressures of H_2 , I_2 , and HI are 0.06443 atm, 0.06540 atm, and 0.4821 atm, respectively. Calculate K_p for the following reaction at this temperature.



- The equilibrium constant, K_p , for the reaction indicated by the following equation is 0.715 at 47°C.



Calculate the partial pressures of N_2O_4 and NO_2 in an experiment in which 3.3 moles of N_2O_4 is placed in a 5.0-L flask and allowed to establish equilibrium at 47°C.

- The equilibrium constant, K_p , is 1.92 at 252°C for the decomposition reaction of phosphorus pentachloride indicated in the following equation.

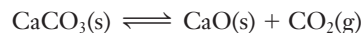


Calculate the partial pressures of all species present after 6.0 moles of PCl_5 is placed in an evacuated 4.0-liter container and equilibrium is reached at 252°C.

- The following equilibrium partial pressures were measured at 750°C: $P_{\text{H}_2} = 0.387$ atm, $P_{\text{CO}_2} = 0.152$ atm, $P_{\text{CO}} = 0.180$ atm, and $P_{\text{H}_2\text{O}} = 0.252$ atm. What is the value of the equilibrium constant, K_p , for the reaction?



- The dissociation of calcium carbonate has an equilibrium constant of $K_p = 1.16$ at 800°C.



- What is K_c for the reaction?
 - If you place 22.5 g of CaCO_3 in a 9.56-L container at 800°C, what is the pressure of CO_2 in the container?
 - What percentage of the original 22.5-g sample of CaCO_3 remains undecomposed at equilibrium?
- For the reaction



$K_p = 2550$. at 4000 K. What is the value of K_c ?

- A stream of gas containing H_2 at an initial partial pressure of 0.200 atm is passed through a tube in which CuO is kept at 500. K. The reaction



comes to equilibrium. For this reaction, $K_p = 1.6 \times 10^9$. What is the partial pressure of H_2 in the gas leaving the tube? Assume that the total pressure of the stream is unchanged.

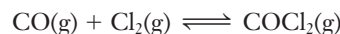
Relationships Among K , ΔG° , ΔH° , and T

- In the distant future, when hydrogen may be cheaper than coal, steel mills may make iron by the reaction



For this reaction, $\Delta H^\circ = 96$ kJ/mol and $K_c = 8.11$ at 1000. K. (a) What percentage of the H_2 remains unreacted after the reaction has come to equilibrium at 1000. K? (b) Is this percentage greater or less if the temperature is decreased to below 1000. K?

- What kind of equilibrium constant can be calculated from a ΔG° value for a reaction involving only gases?
- What must be true of the value of ΔG° for a reaction if (a) $K \gg 1$; (b) $K = 1$; (c) $K \ll 1$?
- A mixture of 3.00 mol of Cl_2 and 3.00 mol of CO is enclosed in a 5.00-L flask at 600.°C. At equilibrium, 3.3% of the Cl_2 has been consumed.



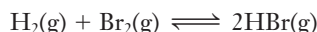
- Calculate K_c for the reaction at 600.°C. (b) Calculate ΔG° for the reaction at this temperature.
- (a) Use the tabulated thermodynamic values of ΔH_f° and S° to calculate the value of K_p at 25°C for the gas-phase reaction



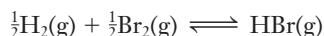
(b) Calculate the value of K_p for this reaction at 200.°C, by the same method as in part (a). (c) Repeat the calculation of part (a) using tabulated values of ΔG_f° .



85. The equilibrium constant K_c for the reaction

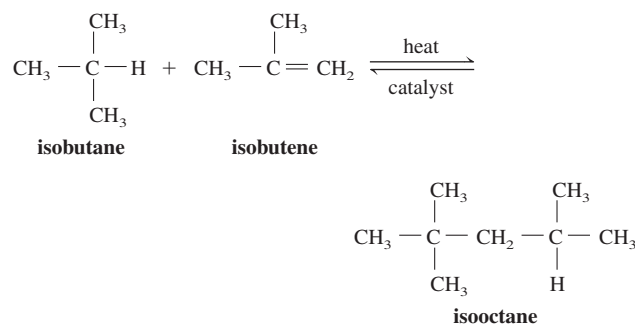


is 1.6×10^5 at 1297 K and 3.5×10^4 at 1495 K. (a) Is ΔH° for this reaction positive or negative? (b) Find K_c for the reaction

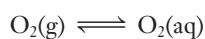


at 1297 K. (c) Pure HBr is placed in a container of constant volume and heated to 1297 K. What percentage of the HBr is decomposed to H_2 and Br_2 at equilibrium?

86. The air pollutant sulfur dioxide can be partially removed from stack gases in industrial processes and converted to sulfur trioxide, the acid anhydride of commercially important sulfuric acid. Write the equation for the reaction, using the smallest whole-number coefficients. Calculate the value of the equilibrium constant for this reaction at 25°C from values of ΔG_f° in Appendix K.
87. The value of ΔH° for the reaction in Exercise 86 is -197.6 kJ/mol. (a) Predict qualitatively (i.e., without calculation) whether the value of K_p for this reaction at 500.°C would be greater than, the same as, or less than the value at room temperature (25°C). (b) Now calculate the value of K_p at 500.°C.
88. ▲ The following is an example of an alkylation reaction that is important in the production of isooctane (2,2,4-trimethylpentane) from two components of crude oil: isobutane and isobutene. Isooctane is an antiknock additive for gasoline. The thermodynamic equilibrium constant, K , for this reaction at 25°C is 4.3×10^6 , and ΔH° is -78.58 kJ/mol.
- Calculate ΔG° at 25°C.
 - Calculate K at 800.°C.
 - Calculate ΔG° at 800.°C.
 - How does the spontaneity of the forward reaction at 800.°C compare with that at 25°C?
 - Why do you think the reaction mixture is heated in the industrial preparation of isooctane?
 - What is the purpose of the catalyst? Does it affect the forward reaction more than the reverse reaction?

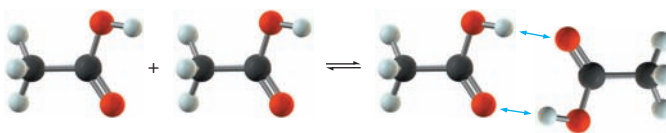


89. ● Oxygen gas dissolves in water to a small extent according to the equilibrium:



Fish extract the dissolved O_2 . Without oxygen in the water, the fish will die. The heating of water in lakes and reservoirs has led to massive fish kills caused by suffocation. Without doing actual calculations, determine from these facts the sign of ΔH for the equilibrium as written above.

90. ▲ In the gas phase, acetic acid forms an equilibrium between the monomer and the dimer:

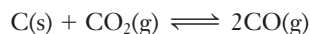


The equilibrium constant for the equation as written is 3.2×10^4 at 25°C. Is the monomer or dimer favored at equilibrium?

91. Describe, in general terms, each of the following reactions and also characterize each as product- or reactant-favored.
- $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g})$ $K_p = 1.2 \times 10^{45}$
 - $\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ $K_p = 9.1 \times 10^{-41}$
 - $\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}(\text{g})$ $K_p = 1.2 \times 10^{-10}$

Mixed Exercises

92. At 700.°C, K_p is 1.50 for the reaction



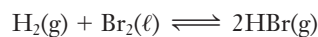
Suppose the total gas pressure at equilibrium is 1.00 atm. What are the partial pressures of CO and CO_2 ?

93. At $-10.$ °C, the solid compound $\text{Cl}_2(\text{H}_2\text{O})_8$ is in equilibrium with gaseous chlorine, water vapor, and ice. The partial pressures of the two gases in equilibrium with a mixture of $\text{Cl}_2(\text{H}_2\text{O})_8$ and ice are 0.20 atm for Cl_2 and 0.00262 atm for water vapor. Find the equilibrium constant K_p for each of these reactions.
- $\text{Cl}_2(\text{H}_2\text{O})_8(\text{s}) \rightleftharpoons \text{Cl}_2(\text{g}) + 8\text{H}_2\text{O}(\text{g})$
 - $\text{Cl}_2(\text{H}_2\text{O})_8(\text{s}) \rightleftharpoons \text{Cl}_2(\text{g}) + 8\text{H}_2\text{O}(\text{s})$
- Why are your two answers so different?
94. A flask contains $\text{NH}_4\text{Cl}(\text{s})$ in equilibrium with its decomposition products



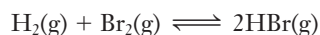
For this reaction, $\Delta H = 176$ kJ/mol. How is the mass of NH_3 in the flask affected by each of the following disturbances? (a) The temperature is decreased. (b) NH_3 is added. (c) HCl is added. (d) NH_4Cl is added, with no appreciable change in the gas volume. (e) A large amount of NH_4Cl is added, decreasing the volume available to the gases.

95. The equilibrium constant for the reaction



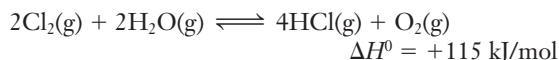
is $K_p = 4.5 \times 10^{18}$ at 25°C. The vapor pressure of liquid Br_2 at this temperature is 0.28 atm.

- (a) Find K_p at 25°C for the reaction



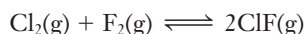
- (b) How will the equilibrium in part (a) be shifted by an increase in the volume of the container if (1) liquid Br₂ is absent, (2) liquid Br₂ is present? Explain why the effect is different in these two cases.

96. Given that K_p is 4.6×10^{-14} at 25°C for the reaction



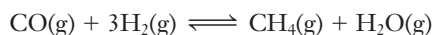
calculate K_p and K_c for the reaction at 400.°C and at 800.°C.

97. $K_c = 19.9$ for the reaction



What will happen in a reaction mixture originally containing $[\text{Cl}_2] = 0.200 \text{ mol/L}$, $[\text{F}_2] = 0.300 \text{ mol/L}$, and $[\text{ClF}] = 0.950 \text{ mol/L}$?

98. A mixture of CO, H₂, CH₄, and H₂O is kept at 1133 K until the reaction



has come to equilibrium. The volume of the container is 0.100 L. The equilibrium mixture contains $1.21 \times 10^{-4} \text{ mol CO}$, $2.47 \times 10^{-4} \text{ mol H}_2$, $1.21 \times 10^{-4} \text{ mol CH}_4$, and $5.63 \times 10^{-8} \text{ mol H}_2\text{O}$. Calculate K_p for this reaction at 1133 K.

99. What would the pressure of hydrogen be at equilibrium when $P_{\text{WCl}_6} = 0.012 \text{ atm}$ and $P_{\text{HCl}} = 0.10 \text{ atm}$? $K_p = 1.37 \times 10^{21}$ at 900. K.



Conceptual Exercises

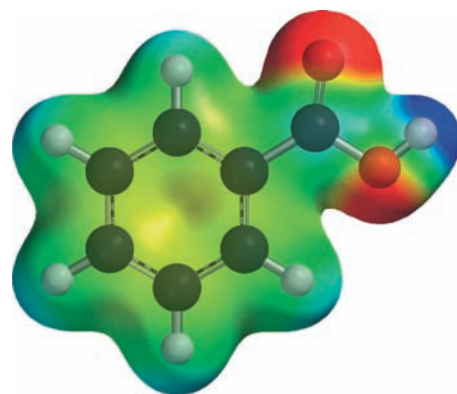
100. When the beam of the triple beam balance stops swinging, has the balance reached a dynamic or a static equilibrium? Explain.



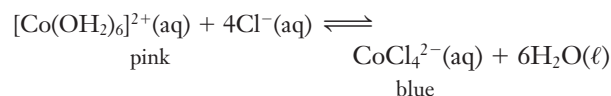
Triple beam balance

101. The term “equilibrium” brings to mind the word “equal.” What is the relationship between the two terms?
102. The masses of participants in a chemical equilibrium are not the same on both sides of the reaction. Does the equilibrium concept violate the Law of Conservation of Matter? Explain.
103. A sample of benzoic acid, a solid carbon-containing acid, is in equilibrium with an aqueous solution of benzoic acid. A tiny quantity of D₂O, water containing

the isotope ²H, deuterium, is added to the solution. The solution is allowed to stand at constant temperature for several hours, after which some of the solid benzoic acid is removed and analyzed. The benzoic acid is found to contain a tiny quantity of deuterium, D, and the formula of the deuterium-containing molecules is C₆H₅COOD. Explain how this can happen. (Hint: Look at the ECP plot.)



104. Imagine yourself the size of atoms and molecules inside a beaker containing the following equilibrium mixture with a K greater than 1.



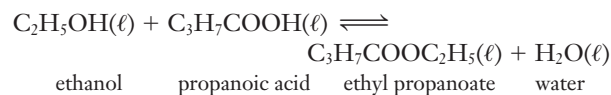
Write a brief description of what you observe around you before and after additional water is added to the mixture.

105. Dinitrogen tetroxide dissociates into nitrogen dioxide:



At 110°C the concentrations of N₂O₄ and NO₂ are approximately equal. If 3.00 mol of dinitrogen tetroxide are placed in a sealed container at 110°C and allowed to come to equilibrium, how much NO₂ will be present at equilibrium?

106. In the process called esterification, an alcohol (like ethanol) reacts with a carboxylic acid (like propanoic acid), producing an ester and water:



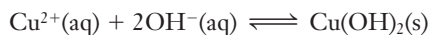
Two (2.00) moles each of ethanol and propanoic acid are combined and the system is allowed to come to equilibrium. At equilibrium, are the amounts of ethanol, propanoic acid, ethyl propanoate, and water 1.00 mol each? Would *any* ethanol be left? If the system takes 45 minutes to come to equilibrium, how long would it take for *all* of the ethanol and propanoic acid to be converted to ethyl propanoate and water?



107. Oh, no! Where's that scrap of paper I wrote the reaction for today's experiment on? What's this? (*unfolding*) Here's where I scribbled the equilibrium constant expression. Great . . . what use is that? Can you figure out what the equation is from this expression?

$$K_c = \frac{[\text{Cu}(\text{NO}_3)_2]^3[\text{NO}]^2}{[\text{HNO}_3]^8}$$

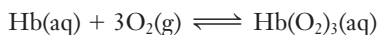
108. When colorless sodium hydroxide solution, NaOH, is added to clear, light blue copper(II) chloride solution, CuCl_2 , a light blue cloud of solid copper(II) hydroxide, $\text{Cu}(\text{OH})_2$, begins to precipitate:



Predict what you would expect to observe when each of the following is added to this equilibrium system: more $\text{Cu}(\text{OH})_2$ solution, more NaOH solution, 1 M aqueous ammonia, NH_3 solution [NH_3 reacts with Cu^{2+} , forming a deep blue ion: $\text{Cu}^{2+} + \text{NH}_3 \longrightarrow \text{Cu}(\text{NH}_3)_4^{2+}$], 0.1 M HCl [H^+ reacts with OH^- , forming water: $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$].

Building Your Knowledge

109. ● Hemoglobin, Hb, has four Fe atoms per molecule that, on the average, pick up roughly three molecules of O_2 .



Discuss mountain (high altitude) or space sickness in terms of this equilibrium.



Astronauts incur the risk of high altitude sickness.

110. The van't Hoff equation can be written as

$$\ln \left(\frac{K_{T_2}}{K_{T_1}} \right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

If $T_2 > T_1$ (the temperature of the reaction increases), how will $\frac{1}{T_2}$ compare with $\frac{1}{T_1}$, and what will be the sign of $\frac{1}{T_1} - \frac{1}{T_2}$? If ΔH° is negative (the reaction is exothermic) and knowing the value of R , what will be the sign of $\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$? Knowing that and the property $\ln \frac{x}{y} = \ln x - \ln y$, compare $\ln K_{T_2}$ with $\ln K_{T_1}$. How does K_{T_2} compare with K_{T_1} ? Is that result consistent with the predictions of LeChatelier's Principle?

111. At 25°C, 550.0 g of deuterium oxide, D_2O (20.0 g/mol; density 1.10 g/mL), and 498.5 g of H_2O (18.0 g/mol; density 0.997 g/mL) are mixed. The volumes are additive. 47.0% of the H_2O reacts to form HDO. Calculate K_c at 25°C for the reaction



112. At its normal boiling point of 100.°C, the heat of vaporization of water is 40.66 kJ/mol. What is the equilibrium vapor pressure of water at 75°C?
113. Use the data in the preceding exercise to calculate the temperature at which the vapor pressure of water is 1.20 atm.

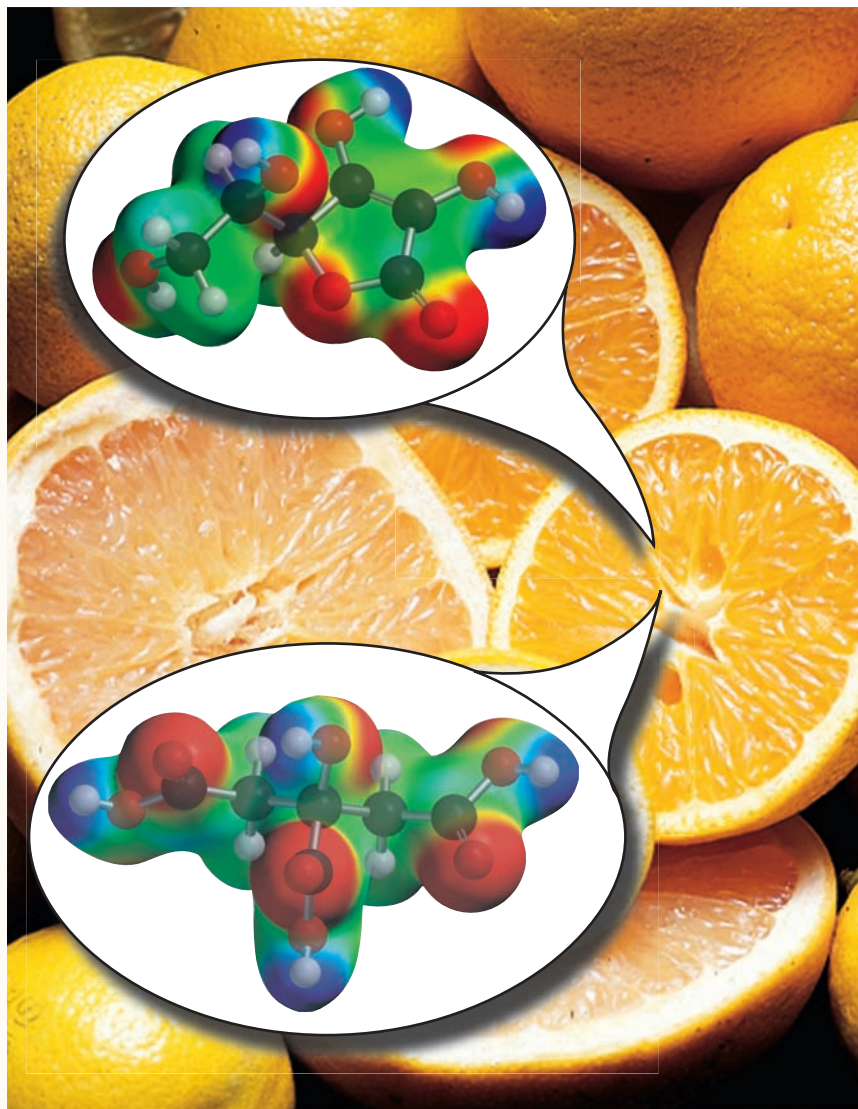
Beyond the Textbook

NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.*

114. Use an internet search engine to locate information on a mission to Mars and equilibrium. (a) What chemical equilibrium is associated with the Mars mission? (b) What factors influence the equilibrium in part (a)?
115. Use an internet search engine to locate information on Max Bodenstein. What equilibrium constant or reaction did he study? What year did he publish his results?
116. Use an internet search engine to locate information on LeChatelier. State his principle in simple terms. Give an example of LeChatelier's Principle being applied to a non-chemical equilibrium.
117. Use an internet search engine to locate information on Karst formations. Describe the reaction that creates a Karst formation. Does that reaction ever establish an equilibrium?

Ionic Equilibria I: Acids and Bases

18



Ascorbic acid (*top*) and citric acid (*bottom*) are two of the weak acids present in oranges and other citrus fruits.

Charles D. Winters

OUTLINE

- 18-1** A Review of Strong Electrolytes
- 18-2** The Autoionization of Water
- 18-3** The pH and pOH Scales
- 18-4** Ionization Constants for Weak Monoprotic Acids and Bases
- 18-5** Polyprotic Acids
- 18-6** Solvolysis
- 18-7** Salts of Strong Bases and Strong Acids
- 18-8** Salts of Strong Bases and Weak Acids
- 18-9** Salts of Weak Bases and Strong Acids
- 18-10** Salts of Weak Bases and Weak Acids
- 18-11** Salts That Contain Small, Highly Charged Cations

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Identify strong electrolytes and calculate concentrations of their ions
- ▶ Understand the autoionization of water
- ▶ Understand the pH and pOH scales
- ▶ Use ionization constants for weak monoprotic acids and bases
- ▶ Discuss the concepts of solvolysis and hydrolysis
- ▶ Describe how polyprotic acids ionize in steps and how to calculate concentrations of all species in solutions of polyprotic acids
- ▶ Apply acid–base equilibrium concepts to salts of strong bases and strong acids
- ▶ Apply acid–base equilibrium concepts to salts of strong bases and weak acids
- ▶ Apply acid–base equilibrium concepts to salts of weak bases and strong acids
- ▶ Apply acid–base equilibrium concepts to salts of weak bases and weak acids
- ▶ Apply acid–base equilibrium concepts to salts of small, highly charged cations

Aqueous solutions are very important. Nearly three-fourths of the earth's surface is covered with water. Enormous numbers of chemical reactions occur in the oceans and smaller bodies of water. Plant and animal fluids are mostly water. Life processes (chemical reactions) of all plants and animals occur in aqueous solutions or in contact with water. Before we were born, all of us developed in sacs filled with aqueous solutions, which protected and helped nurture us until we had developed to the point that we could live in the atmosphere.

18-1 A Review of Strong Electrolytes

In previous discussions we have seen that water-soluble compounds may be classified as either electrolytes or nonelectrolytes. **Electrolytes** are compounds that ionize (or dissociate into their constituent ions) to produce aqueous solutions that conduct an electric current. **Nonelectrolytes** exist as molecules in aqueous solution, and such solutions do not conduct an electric current.

Strong electrolytes are ionized or dissociated completely, or very nearly completely, in dilute aqueous solutions. Strong electrolytes include strong acids, strong bases, and most soluble salts. You should review the discussions of these substances in Sections 6-1 and 10-8. Some strong acids and strong bases are listed again in Table 18-1. See Section 6-1, Part 5, for the solubility guidelines for ionic compounds.

Concentrations of ions in aqueous solutions of strong electrolytes can be calculated directly from the molarity of the strong electrolyte, as the following example illustrates.

Table 18-1 Some Strong Acids and Strong Bases

Strong Acids	
HCl	HNO ₃
HBr	HClO ₄
HI	(HClO ₃)*
	H ₂ SO ₄
Strong Bases	
LiOH	
NaOH	
KOH	Ca(OH) ₂
RbOH	Sr(OH) ₂
CsOH	Ba(OH) ₂

*Chloric acid, HClO₃, is sometimes not included in a list of strong acids since it is not commonly encountered. However, its anion is much more common.

EXAMPLE 18-1 Calculation of Concentrations of Ions

Calculate the molar concentrations of Ba²⁺ and OH⁻ ions in 0.030 M barium hydroxide.

Plan

Write the equation for the dissociation of Ba(OH)₂, and construct the reaction summary. Ba(OH)₂ is a strong base that is completely dissociated.

Solution

From the equation for the dissociation of barium hydroxide, we see that *one* mole of Ba(OH)₂ produces *one* mole of Ba²⁺ ions and *two* moles of OH⁻ ions.

(strong base)	$\text{Ba(OH)}_2(\text{s})$	$\longrightarrow$	$\text{Ba}^{2+}(\text{aq})$	+	$2\text{OH}^{-}(\text{aq})$
initial	0.030 M				
change due to rxn	-0.030 M		+0.030 M		+2(0.030) M
final	0 M		0.030 M		0.060 M

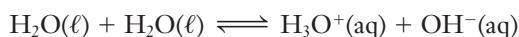
$$[\text{Ba}^{2+}] = 0.030 \text{ M} \quad \text{and} \quad [\text{OH}^{-}] = 0.060 \text{ M}$$

You should now work Exercises 4 and 6.

► Recall that we use a single arrow ($\longrightarrow$) to indicate that a reaction goes to completion, or nearly to completion, in the indicated direction.

18-2 The Autoionization of Water

Careful experiments on its electrical conductivity have shown that pure water ionizes to a very slight extent.



Because the H_2O is pure, its activity is 1, so we do not include its concentration in the equilibrium constant expression. This equilibrium constant is known as the **ion product for water** and is usually represented as K_w .

$$K_w = [\text{H}_3\text{O}^{+}][\text{OH}^{-}]$$

The formation of each H_3O^{+} ion by the ionization of water is always accompanied by the formation of an OH^{-} ion. Thus, in *pure* water the concentration of H_3O^{+} is *always* equal to the concentration of OH^{-} . Careful measurements show that, in pure water at 25°C ,

$$[\text{H}_3\text{O}^{+}] = [\text{OH}^{-}] = 1.0 \times 10^{-7} \text{ mol/L}$$

Substituting these concentrations into the K_w expression gives

$$\begin{aligned} K_w &= [\text{H}_3\text{O}^{+}][\text{OH}^{-}] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) \\ &= 1.0 \times 10^{-14} \quad (\text{at } 25^{\circ}\text{C}) \end{aligned}$$

Although the expression $K_w = [\text{H}_3\text{O}^{+}][\text{OH}^{-}] = 1.0 \times 10^{-14}$ was obtained for pure water, *it is also valid for dilute aqueous solutions at 25°C* . This is one of the most useful relationships chemists have discovered. It gives a simple relationship between H_3O^{+} and OH^{-} concentrations in *all* dilute aqueous solutions.

The *value* of K_w is different at different temperatures (Table 18-2), but the *relationship* $K_w = [\text{H}_3\text{O}^{+}][\text{OH}^{-}]$ is still valid.

► Recall that we use a double arrow ($\rightleftharpoons$) to indicate that the reaction can go in either direction to reach equilibrium.

► Solutions in which the concentration of solute is less than about 1 mol/L are usually called dilute solutions.

In this text, we shall assume a temperature of 25°C for all calculations involving aqueous solutions unless we specify another temperature.

EXAMPLE 18-2 Calculation of Ion Concentrations

Calculate the concentrations of H_3O^{+} and OH^{-} ions in a 0.050 M HNO_3 solution.

Plan

Write the equation for the ionization of HNO_3 , a strong acid, and construct the reaction summary, which gives the concentrations of H_3O^{+} (and NO_3^{-}) ions directly. Then use the relationship $K_w = [\text{H}_3\text{O}^{+}][\text{OH}^{-}] = 1.0 \times 10^{-14}$ to find the concentration of OH^{-} ions.

Table 18-2 K_w at Some Temperatures

Temperature ($^{\circ}\text{C}$)	K_w
0	1.1×10^{-15}
10	2.9×10^{-15}
25	1.0×10^{-14}
37*	2.4×10^{-14}
45	4.0×10^{-14}
60	9.6×10^{-14}

*Normal human body temperature.

Unless otherwise noted, all content on this page is © Cengage Learning.

STOP & THINK

The initial H_3O^+ concentration is actually $1 \times 10^{-7} \text{ M}$, which is the contribution from water. This is negligible compared to the 0.050 M H_3O^+ from the nitric acid.

► In the remainder of this textbook we will be working nearly exclusively with aqueous solutions, so we will often omit the "(aq)" and "(ℓ)."

STOP & THINK

Recall that $[\text{OH}^-]_{\text{from H}_2\text{O}} = [\text{H}_3\text{O}^+]_{\text{from H}_2\text{O}}$ in *all* aqueous solutions. So we know that $[\text{H}_3\text{O}^+]_{\text{from H}_2\text{O}}$ must also be $2.0 \times 10^{-13} \text{ M}$. The 2.0×10^{-13} is only negligible when it is added to or subtracted from a number that is at least two orders of magnitude larger.

Solution

The reaction summary for the ionization of HNO_3 , a strong acid, is

(strong acid)	HNO_3	+	H_2O	$\longrightarrow$	H_3O^+	+	NO_3^-
initial	0.050 M				$\approx 0 \text{ M}$		0 M
change due to rxn	-0.050 M				$+0.050 \text{ M}$		$+0.050 \text{ M}$
at equil	0 M				0.050 M		0.050 M

$$[\text{H}_3\text{O}^+] = [\text{NO}_3^-] = 0.050 \text{ M}$$

The $[\text{OH}^-]$ is determined from the equation for the autoionization of water and its K_w . The initial value for $[\text{H}_3\text{O}^+]$ is 0.050 M from the dissociation of the nitric acid. We assume that the initial concentration of OH^- from water is $1 \times 10^{-7} \text{ M}$, which is negligible and is approximated as zero.

	$2\text{H}_2\text{O}$	$\rightleftharpoons$	H_3O^+	+	OH^-
initial			0.050 M		$\approx 0 \text{ M}$
change due to rxn	$-2x \text{ M}$		$+x \text{ M}$		$+x \text{ M}$
at equil			$(0.050 + x) \text{ M}$		$x \text{ M}$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$1.0 \times 10^{-14} = (0.050 + x)(x)$$

Because the product $(0.050 + x)(x)$ is a very small number, we know that x must be very small. Thus, it will not matter whether we add x to 0.050 ; we can assume that $(0.050 + x) \approx 0.050$. This simplifies the math considerably and we can substitute this approximation into the equation and solve.

$$1.0 \times 10^{-14} = (0.050)(x) \quad \text{or} \quad x = \frac{1.0 \times 10^{-14}}{0.050} = 2.0 \times 10^{-13} \text{ M} = [\text{OH}^-]$$

We see that the assumption that x is much smaller than 0.050 was a good one.

You should now work Exercise 14.

In solving Example 18-2 we assumed that *all* of the H_3O^+ (0.050 M) came from the ionization of HNO_3 and neglected the H_3O^+ formed by the ionization of H_2O . The ionization of H_2O produces only $2.0 \times 10^{-13} \text{ M}$ H_3O^+ and $2.0 \times 10^{-13} \text{ M}$ OH^- in *this solution*. Adding $2.0 \times 10^{-13} \text{ M}$ H_3O^+ from the ionization of water to the 0.050 M H_3O^+ from the nitric acid gives a total H_3O^+ concentration of $0.05000000000002 \text{ M}$. The difference is negligible relative to 0.050 M H_3O^+ from the nitric acid. Thus, we were justified in assuming that the $[\text{H}_3\text{O}^+]$ is derived solely from the strong acid. An easier way to carry out the calculation to find the $[\text{OH}^-]$ concentration is to write directly

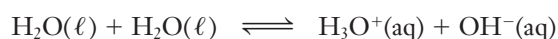
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad \text{or} \quad [\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]}$$

Then we substitute to obtain

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{0.050} = 2.0 \times 10^{-13} \text{ M}$$

From now on, we shall use this more direct approach for such calculations.

When nitric acid is added to water, large numbers of H_3O^+ ions are produced. The large increase in $[\text{H}_3\text{O}^+]$ shifts the water ionization equilibrium far to the left (LeChatelier's Principle), and the $[\text{OH}^-]$ decreases.



In acidic solutions the H_3O^+ concentration is always greater than the OH^- concentration. We should not conclude that acidic solutions contain no OH^- ions. Rather, the $[\text{OH}^-]$ is always less than $1.0 \times 10^{-7} \text{ M}$ in such solutions. The reverse is true for basic so-

lutions, in which the $[\text{OH}^-]$ is always greater than $1.0 \times 10^{-7} \text{ M}$. By definition, “neutral” aqueous solutions at 25°C are solutions in which $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$.

Solution	General Condition	At 25°C (M)	
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	$[\text{H}_3\text{O}^+] > 1.0 \times 10^{-7}$	$[\text{OH}^-] < 1.0 \times 10^{-7}$
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$	$[\text{OH}^-] = 1.0 \times 10^{-7}$
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	$[\text{H}_3\text{O}^+] < 1.0 \times 10^{-7}$	$[\text{OH}^-] > 1.0 \times 10^{-7}$

18-3 The pH and pOH Scales

The pH and pOH scales provide a convenient way to express the acidity and basicity of dilute aqueous solutions. The **pH** and **pOH** of a solution are defined as

$$\begin{array}{ll} \text{pH} = -\log [\text{H}_3\text{O}^+] & \text{or} \quad [\text{H}_3\text{O}^+] = 10^{-\text{pH}} \\ \text{pOH} = -\log [\text{OH}^-] & \text{or} \quad [\text{OH}^-] = 10^{-\text{pOH}} \end{array}$$

Note that we write pH rather than pH_3O . At the time the pH concept was developed, H_3O^+ was represented as H^+ . Various “p” terms are used in chemistry and other sciences. In general a lowercase “p” before a symbol means “negative logarithm of the symbol.” Thus, pH is the negative logarithm of the H_3O^+ concentration, **pOH** is the negative logarithm of the OH^- concentration, and **pK** refers to the negative logarithm of an equilibrium constant. It is convenient to describe the autoionization of water in terms of **pK_w**.

► When dealing with pH, we always use the base-10 (common) logarithm, *not* the base-e (natural) logarithm. This is because pH is *defined* using base-10 logarithms.

$$\text{pK}_w = -\log K_w \quad (= 14.0 \text{ at } 25^\circ\text{C})$$

EXAMPLE 18-3 Calculation of pH

Calculate the pH of a solution in which the H_3O^+ concentration is 0.050 mol/L .

Plan

We are given the value for $[\text{H}_3\text{O}^+]$; so we take the negative logarithm of this value.

Solution

$$\begin{aligned} [\text{H}_3\text{O}^+] &= 0.050 \text{ M} = 5.0 \times 10^{-2} \text{ M} \\ \text{pH} &= -\log [\text{H}_3\text{O}^+] = -\log [5.0 \times 10^{-2}] = 1.30 \end{aligned}$$

This answer contains only *two* significant figures. The “1” in 1.30 is *not* a significant figure; it comes from the power of ten.

You should now work Exercise 22.

STOP & THINK
In a pH value, only the digits after the decimal point are significant figures.

EXAMPLE 18-4 Calculation of H_3O^+ Concentration from pH

The pH of a solution is 3.301. What is the concentration of H_3O^+ in this solution?

Plan

By definition, $\text{pH} = -\log [\text{H}_3\text{O}^+]$. We are given the pH, so we solve for $[\text{H}_3\text{O}^+]$.

Solution

From the definition of pH, we write

$$-\log [\text{H}_3\text{O}^+] = 3.301$$

► On most calculators the antilog function is indicated by a 10^x key (where $x = -3.301$ for this problem).

Multiplying through by -1 gives

$$\log [\text{H}_3\text{O}^+] = -3.301$$

Taking the inverse logarithm (antilog) of both sides of the equation gives

$$[\text{H}_3\text{O}^+] = 10^{-3.301} \quad \text{so} \quad [\text{H}_3\text{O}^+] = 5.00 \times 10^{-4} \text{ M}$$

You should now work Exercise 24.

A convenient relationship between pH and pOH in *all dilute solutions at 25°C* can be easily derived. We start with the K_w expression.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Taking the logarithm of both sides of this equation gives

$$\log [\text{H}_3\text{O}^+] + \log [\text{OH}^-] = \log (1.0 \times 10^{-14})$$

Multiplying both sides of this equation by -1 gives

$$(-\log [\text{H}_3\text{O}^+]) + (-\log [\text{OH}^-]) = -\log (1.0 \times 10^{-14})$$

or

$$\text{pH} + \text{pOH} = 14.00$$

We can now relate $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$, as well as pH and pOH.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad \text{and} \quad \text{pH} + \text{pOH} = 14.00 \quad (\text{at } 25^\circ\text{C})$$

From this relationship, we see that pH and pOH can *both* be positive only if *both* are less than 14. If either pH or pOH is greater than 14, the other is obviously negative.

Please study carefully the following summary. It will be helpful.

Solution	General Condition	At 25°C
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$ $\text{pH} < \text{pOH}$	$[\text{H}_3\text{O}^+] > 1.0 \times 10^{-7} \text{ M} > [\text{OH}^-]$ $\text{pH} < 7.00 < \text{pOH}$
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$ $\text{pH} = \text{pOH}$	$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M} = [\text{OH}^-]$ $\text{pH} = 7.00 = \text{pOH}$
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$ $\text{pH} > \text{pOH}$	$[\text{H}_3\text{O}^+] < 1.0 \times 10^{-7} \text{ M} < [\text{OH}^-]$ $\text{pH} > 7.00 > \text{pOH}$

To develop familiarity with the pH and pOH scales, consider a series of solutions in which $[\text{H}_3\text{O}^+]$ varies from 10 M to $1.0 \times 10^{-15} \text{ M}$. Obviously, $[\text{OH}^-]$ will vary from $1.0 \times 10^{-15} \text{ M}$ to 10 M in these solutions. Table 18-3 summarizes these scales.

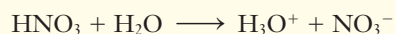
EXAMPLE 18-5 pH and pOH of an Acidic Solution

Calculate $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH for a 0.015 M HNO_3 solution.

Plan

We write the equation for the ionization of the strong acid, HNO_3 , which gives us $[\text{H}_3\text{O}^+]$. Then we calculate pH. We use the relationships $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ and $\text{pH} + \text{pOH} = 14.00$ to find pOH and $[\text{OH}^-]$.

STOP & THINK
These are very important relationships. Remember them!

Solution

Because nitric acid is a strong acid (it ionizes completely), we know that

$$[\text{H}_3\text{O}^+] = 0.015 \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.015) = -(-1.82) = 1.82$$

We also know that $\text{pH} + \text{pOH} = 14.00$. Therefore,

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 1.82 = 12.18$$

Because $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$, $[\text{OH}^-]$ is easily calculated.

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.015} = 6.7 \times 10^{-13} \text{ M}$$

You should now work Exercise 25.

► All ions are hydrated in aqueous solution. We often omit the designations (*ℓ*), (*g*), (*s*), (*aq*), and so on.

STOP & THINK

It is easy to confuse pH and pOH because pH values are far more commonly used. Here $\text{pOH} = 12.18$, which might initially lead someone thinking only about pH's to conclude that the solution is basic. But as one can see from the very small $[\text{OH}^-]$ value and pH of 1.82, the solution is definitely acidic.

pH Range for a Few Common Substances

Substance	pH Range
Gastric contents (human)	1.6–3.0
Soft drinks	2.0–4.0
Lemons	2.2–2.4
Vinegar	2.4–3.4
Tomatoes	4.0–4.4
Beer	4.0–5.0
Urine (human)	4.8–8.4
Milk (cow's)	6.3–6.6
Saliva (human)	6.5–7.5
Blood plasma (human)	7.3–7.5
Egg white	7.6–8.0
Milk of magnesia	10.5
Household ammonia	11–12

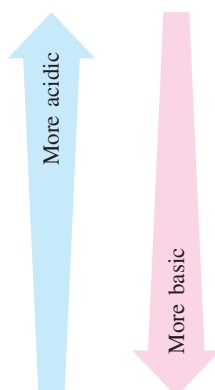


Table 18-3 Relationships Among $[\text{H}_3\text{O}^+]$, pH, pOH, and $[\text{OH}^-]$

$[\text{H}_3\text{O}^+]$	pH		pOH	$[\text{OH}^-]$
10^{-15}	15		-1	10^1
10^{-14}	14		0	1
10^{-13}	13		1	10^{-1}
10^{-12}	12		2	10^{-2}
10^{-11}	11		3	10^{-3}
10^{-10}	10		4	10^{-4}
10^{-9}	9		5	10^{-5}
10^{-8}	8		6	10^{-6}
10^{-7}	7		7	10^{-7}
10^{-6}	6		8	10^{-8}
10^{-5}	5		9	10^{-9}
10^{-4}	4		10	10^{-10}
10^{-3}	3		11	10^{-11}
10^{-2}	2		12	10^{-12}
10^{-1}	1		13	10^{-13}
1	0		14	10^{-14}
10^1	-1		15	10^{-15}

H_3O^+ concentration

OH^- concentration

Increasing basicity

Neutral

Increasing acidity

STOP & THINK

Note that the pH can be 0 or a small negative number for concentrated strong acid solutions. A $\text{pH} = -1.0$ represents $[\text{H}^+] = 10.0 \text{ M}$, which is certainly possible for a concentrated strong acid. But $\text{pH} = -2.0$ indicates a solution with $[\text{H}^+] = 100.0 \text{ M}$, which is not possible.

STOP & THINK

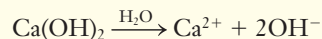
When asked for the pH of a basic solution, you should usually first work out the pOH value. It is very important to remember to then subtract the pOH value from 14.0 to calculate the pH. You should also remember the simple concept that the pH for a basic solution is greater than 7.0.

EXAMPLE 18-6 Calculations Involving pH and pOH

Calculate $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH for a 0.015 M $\text{Ca}(\text{OH})_2$ solution.

Plan

We write the equation for the ionization of the strong base $\text{Ca}(\text{OH})_2$, which gives us $[\text{OH}^-]$. Then we calculate pOH. We use the relationships $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ and $\text{pH} + \text{pOH} = 14.00$ to find pH and $[\text{H}_3\text{O}^+]$.

Solution

Because calcium hydroxide is a strong base (it dissociates completely), we know that

$$[\text{OH}^-] = 2 \times 0.015 \text{ M} = 0.030 \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (0.030) = -(-1.52) = 1.52$$

We also know that $\text{pH} + \text{pOH} = 14.00$. Therefore,

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.52 = 12.48$$

Because $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$, $[\text{H}_3\text{O}^+]$ is easily calculated.

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.030} = 3.3 \times 10^{-13} \text{ M}$$

You should now work Exercises 26 and 37.

► A pH meter is much more accurate than an indicator for obtaining pH values.

The pH of a solution can be determined using a pH meter (Figure 18-1) or by the indicator method. Acid–base **indicators** are intensely colored complex organic compounds that are different colors in solutions of different pH (see Section 19-4). Many are weak acids or weak bases that are useful over rather narrow ranges of pH values. *Universal indicators* are mixtures of several indicators; they show several color changes over a wide range of pH values.

In the indicator method, we prepare a series of solutions of known pH (standard solutions). We add a universal indicator to each; solutions with different pH values turn different colors (Figure 18-2). We then add the same universal indicator to the unknown solution and compare its color to those of the standard solutions. Solutions with the same pH have the same color.

Universal indicator papers can also be used to determine pH. A drop of solution is placed on a piece of paper or a piece of the paper is dipped into a solution. The color of the paper is then compared with a color chart on the container to establish the pH of the solution.

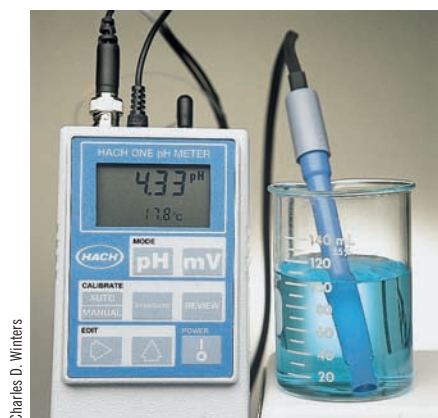


Figure 18-1 A pH meter gives the pH of a solution directly. When the electrode is dipped into a solution, the meter displays the pH. The pH meter is based on the glass electrode. This sensing device generates a voltage that is proportional to the pH of the solution in which the electrode is placed. The instrument has an electrical circuit to amplify the voltage from the electrode and a meter that relates the voltage to the pH of the solution. Before being used, a pH meter should be calibrated with a series of solutions of known pH.

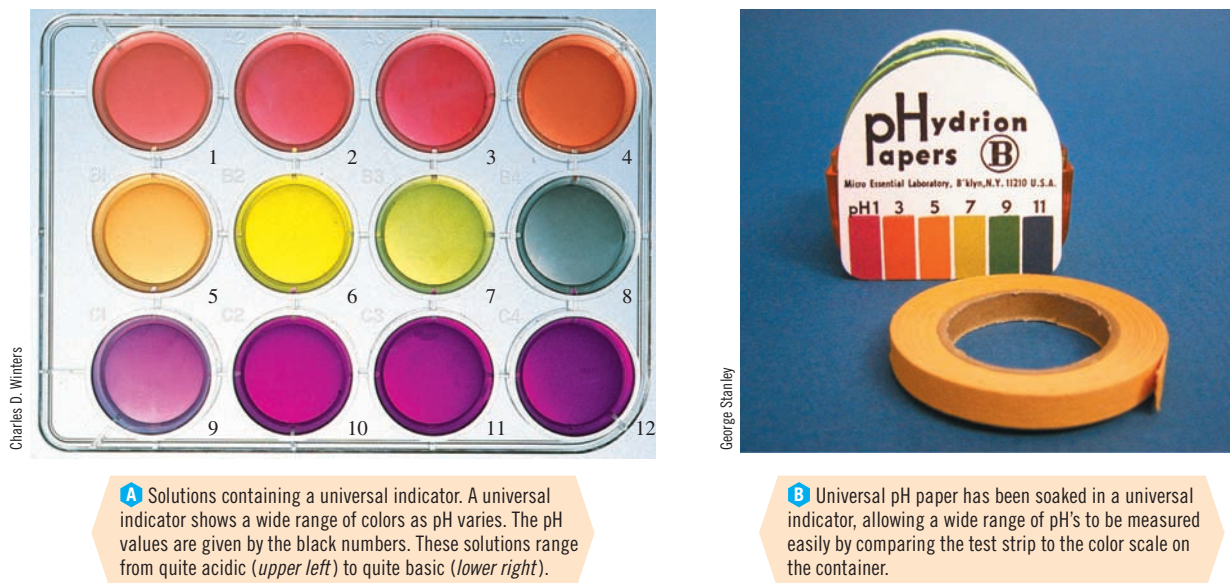


Figure 18-2

18-4 Ionization Constants for Weak Monoprotic Acids and Bases

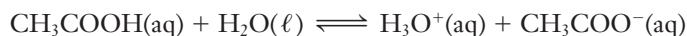
We have discussed strong acids and strong bases. There are relatively few of these. Weak acids are much more numerous than strong acids. For this reason you were asked to learn the list of common strong acids (see Table 18-1). You may assume that other acids you encounter in this text will be weak acids. Table 18-4 contains names, formulas, ionization constants, and pK_a values for a few common weak acids; Appendix F contains a longer list of K_a values. *Weak* acids ionize only slightly in dilute aqueous solution. Our classification of acids as strong or weak is based on the *extent to which they ionize in dilute aqueous solution*.

Several weak acids are familiar to us. Vinegar is a 5% solution of acetic acid, CH_3COOH . Carbonated beverages are saturated solutions of carbon dioxide in water, which produces carbonic acid.



Citrus fruits contain citric acid, $\text{C}_3\text{H}_5\text{O}(\text{COOH})_3$. Some ointments and powders used for medicinal purposes contain boric acid, H_3BO_3 . These everyday uses of weak acids suggest that there is a significant difference between strong and weak acids. The difference is that *strong acids ionize completely in dilute aqueous solution, whereas weak acids ionize only slightly*.

Let us consider the reaction that occurs when a weak acid, such as acetic acid, is dissolved in water. The equation for the ionization of acetic acid is



The equilibrium constant for this reaction could be represented as

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]}$$

We should recall that the thermodynamic definition of K is in terms of activities. In dilute solutions, the activity of the (nearly) pure H_2O is essentially 1. The activity of each dissolved species is numerically equal to its molar concentration. Thus the **ionization constant** of a weak acid, K_a , does not include a term for the concentration of water.



The pH of some common substances is shown by a universal indicator. Refer to Figure 18-2 to interpret the indicator colors.

► How can you tell that carbonated beverages are *saturated* CO_2 solutions?

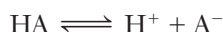
► A **monoprotic acid** has only one ionizable H.

$$\text{p}K_a = -\log K_a$$

Table 18-4 Ionization Constants and $\text{p}K_a$ Values for Some Weak Monoprotic Acids

Acid	Ionization Reaction	K_a at 25°C	$\text{p}K_a$
hydrofluoric acid	$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^-$	7.2×10^{-4}	3.14
nitrous acid	$\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$	4.5×10^{-4}	3.35
acetic acid	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$	1.8×10^{-5}	4.74
hypochlorous acid	$\text{HOCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OCl}^-$	3.5×10^{-8}	7.45
hydrocyanic acid	$\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CN}^-$	4.0×10^{-10}	9.40

We often use HA as a general representation for a monoprotic acid and A^- for its conjugate base. The equation for the ionization of a weak acid can be written as



For example, for acetic acid, we can write either

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

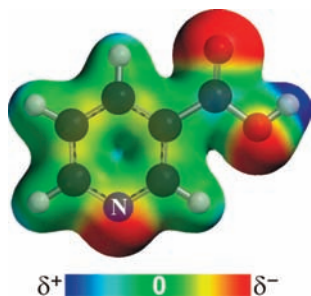
or

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

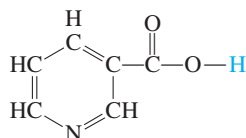
► The value of K_a can be found in Table 18-4.

This expression tells us that in dilute aqueous solutions of acetic acid, the concentration of H_3O^+ multiplied by the concentration of CH_3COO^- and then divided by the concentration of *nonionized* acetic acid is equal to 1.8×10^{-5} .

Ionization constants for weak acids (and bases) must be calculated from *experimentally determined data*. Measurements of pH, conductivity, or depression of freezing point provide data from which these constants can be calculated.



► The structure of nicotinic acid is



Nicotinic acid, also called niacin, is a necessary vitamin in our diets. It is not physiologically related to nicotine.

EXAMPLE 18-7 Calculation of K_a and $\text{p}K_a$ from Equilibrium Concentrations

Nicotinic acid is a weak monoprotic organic acid that we can represent as HA.

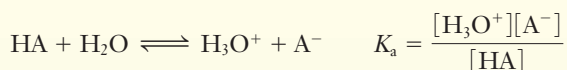


A dilute solution of nicotinic acid was found to contain the following concentrations at equilibrium at 25°C. What are the K_a and $\text{p}K_a$ values? $[\text{HA}] = 0.049 \text{ M}$; $[\text{H}_3\text{O}^+] = [\text{A}^-] = 8.4 \times 10^{-4} \text{ M}$.

Plan

We are given *equilibrium* concentrations, so we substitute these into the expression for K_a .

Solution



$$K_a = \frac{(8.4 \times 10^{-4})(8.4 \times 10^{-4})}{0.049} = 1.4 \times 10^{-5}$$

The equilibrium constant expression is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = 1.4 \times 10^{-5} \quad \text{p}K_a = -\log(1.4 \times 10^{-5}) = 4.85$$

You should now work Exercise 30.

EXAMPLE 18-8 Calculation of K_a from Percent Ionization

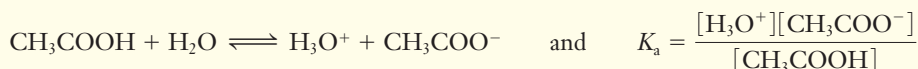
In 0.0100 M solution, acetic acid is 4.2% ionized. Calculate its ionization constant.

Plan

We write the equation for the ionization of acetic acid and its equilibrium constant expression. Next we use the percent ionization to complete the reaction summary and then substitute into the K_a expression.

Solution

The equations for the ionization of CH_3COOH and its ionization constant are



Because 4.2% of the CH_3COOH ionizes,

$$M_{\text{CH}_3\text{COOH}} \text{ that ionizes} = 0.042 \times 0.0100 M = 4.2 \times 10^{-4} M$$

Each mole of CH_3COOH that ionizes forms one mole of H_3O^+ and one mole of CH_3COO^- . We represent this in the reaction summary.

	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons$	H_3O^+	+	CH_3COO^-
initial	0.0100 M	$\approx 0 M$		0 M
change	$-4.2 \times 10^{-4} M$	$+4.2 \times 10^{-4} M$		$+4.2 \times 10^{-4} M$
at equil	$9.58 \times 10^{-3} M$	$4.2 \times 10^{-4} M$		$4.2 \times 10^{-4} M$

Substitution of these values into the K_a expression gives the value for K_a .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(4.2 \times 10^{-4})(4.2 \times 10^{-4})}{9.58 \times 10^{-3}} = 1.8 \times 10^{-5}$$

You should now work Exercise 38.

STOP & THINK

The acetic acid concentration at equilibrium is represented algebraically by $(0.0100 M - x)$. We did not ignore the x value in this case because it was within two orders of magnitude of the number from which it was being subtracted.
 $0.0100 - 0.00042 = 0.00958$
 or $9.58 \times 10^{-3} M$

EXAMPLE 18-9 Calculation of K_a from pH

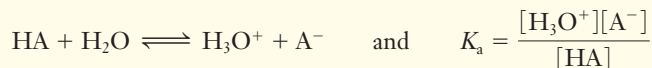
The pH of a 0.115 M solution of chloroacetic acid, ClCH_2COOH , is measured to be 1.92. Calculate K_a for this weak monoprotic acid.

Plan

For simplicity, we represent ClCH_2COOH as HA. We write the ionization equation and the expression for K_a . Next we calculate $[\text{H}_3\text{O}^+]$ for the given pH and complete the reaction summary. Finally, we substitute into the K_a expression.

Solution

The ionization of this weak monoprotic acid and its ionization constant expression may be represented as



We calculate $[\text{H}_3\text{O}^+]$ from the definition of pH.

$$\begin{aligned} \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ [\text{H}_3\text{O}^+] &= 10^{-\text{pH}} = 10^{-1.92} = 0.012 M \end{aligned}$$

We use the usual reaction summary as follows. At this point, we know the *original* $[\text{HA}]$ and the *equilibrium* $[\text{H}_3\text{O}^+]$. From this information, we fill out the “change” line and then deduce the other equilibrium values.

	$\text{HA} + \text{H}_2\text{O} \rightleftharpoons$	H_3O^+	+	A^-
initial	0.115 M	$\approx 0 M$		0 M
change due to rxn	$-0.012 M$	$+0.012 M$		$+0.012 M$
at equil	0.103 M	0.012 M		0.012 M



Charles Steele

Some common household weak acids. A strip of paper impregnated with a universal indicator is convenient for estimating the pH of a solution.

STOP & THINK

Note that because you were given the H_3O^+ concentration in the form of a pH, there are no x values to solve for, just the K_a value. This is, therefore, a very simple problem so long as you convert the pH to the H_3O^+ concentration and are careful to set up the balanced equation with the initial change due to rxn, and at equil values correctly.

Now that all concentrations are known, K_a can be calculated.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.012)(0.012)}{0.103} = 1.4 \times 10^{-3}$$

You should now work Exercise 40.

Problem-Solving Tip Filling in Reaction Summaries

In Examples 18-8 and 18-9, the value of an equilibrium concentration was used to determine the change in concentration. You should become proficient at using a variety of data to determine values that are related via a chemical equation. Let's review what we did in Example 18-9. Only the equilibrium expression, initial concentrations, and the equilibrium concentration of H_3O^+ were known when we started the reaction summary. The following steps show how we filled in the remaining values in the order indicated by the numbered red arrows.

1. $[\text{H}_3\text{O}^+]_{\text{equil}} = 0.012 \text{ M}$, so we record this value
2. $[\text{H}_3\text{O}^+]_{\text{initial}} \approx 0$, so change in $[\text{H}_3\text{O}^+]$ due to rxn must be $+0.012 \text{ M}$
3. Formation of $0.012 \text{ M H}_3\text{O}^+$ consumes 0.012 M HA , so the change in $[\text{HA}] = -0.012 \text{ M}$
4. $[\text{HA}]_{\text{equil}} = [\text{HA}]_{\text{orig}} + [\text{HA}]_{\text{chg}} = 0.115 \text{ M} + (-0.012 \text{ M}) = 0.103 \text{ M}$
5. Formation of $0.012 \text{ M H}_3\text{O}^+$ also gives 0.012 M A^-
6. $[\text{A}^-]_{\text{equil}} = [\text{A}^-]_{\text{orig}} + [\text{A}^-]_{\text{chg}} = 0 \text{ M} + 0.012 \text{ M} = 0.012 \text{ M}$

At equilibrium, $[\text{H}_3\text{O}^+] = 0.012 \text{ M}$ so

	HA	+ H ₂ O	⇌	H ₃ O ⁺	+	A ⁻
initial	0.115 M			0 M		0 M
change due to rxn	-0.012 M			+0.012 M		0.012 M
at equil	0.103 M			0.012 M		0.012 M

Ionization constants are equilibrium constants for ionization reactions, so their values indicate the extents to which weak electrolytes ionize. At the same concentrations, acids with larger ionization constants ionize to greater extents (and are stronger acids) than acids with smaller ionization constants. From Table 18-4, we see that the order of decreasing acid strength for these five weak acids is

(strongest acid) $\text{HF} > \text{HNO}_2 > \text{CH}_3\text{COOH} > \text{HOCl} > \text{HCN}$ (weakest acid)

Conversely, in Brønsted–Lowry terminology (see Section 10-4), the order of increasing base strength of the anions of these acids (their conjugate bases) is

(weakest base) $\text{F}^- < \text{NO}_2^- < \text{CH}_3\text{COO}^- < \text{OCl}^- < \text{CN}^-$ (strongest base)

If we know the value of the ionization constant for a weak acid, we can calculate the concentrations of the species present in solutions of known initial concentrations.

EXAMPLE 18-10 Calculation of Concentrations from K_a

(a) Calculate the concentrations of the various species in 0.10 M hypochlorous acid, HOCl . For HOCl , $K_a = 3.5 \times 10^{-8}$. (b) What is the pH of this solution?

Plan

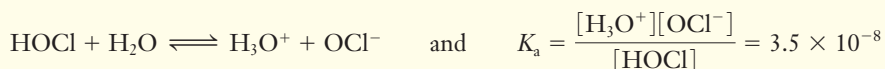
We write the equation for the ionization of the weak acid and its K_a expression. Then we represent the *equilibrium* concentrations algebraically and substitute into the K_a expression. Then we solve for the concentrations and the pH.

► Recall that in Brønsted–Lowry terminology, an acid forms its conjugate base by losing a H^+ .

► We can write the formula for hypochlorous acid as HOCl rather than HClO to emphasize that its structure is $\text{H}-\text{O}-\text{Cl}$.

Solution

(a) The equation for the ionization of HOCl and its K_a expression are



We would like to know the concentrations of H_3O^+ , OCl^- , and nonionized HOCl in solution. An algebraic representation of concentrations is required because there is no other obvious way to obtain the concentrations.

Let $x = \text{mol/L}$ of HOCl that ionizes. Then write the “change” line and complete the reaction summary.

	HOCl	+	H ₂ O	$\rightleftharpoons$	H ₃ O ⁺	+	OCl ⁻
initial	0.10 M				≈ 0 M		0 M
change due to rxn	-x M				+x M		+x M
at equil	(0.10 - x) M				x M		x M

Substituting these algebraic representations into the K_a expression gives

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{(x)(x)}{(0.10 - x)} = 3.5 \times 10^{-8}$$

This is a quadratic equation, but it is not necessary to solve it by the quadratic formula. The small value of the equilibrium constant, K_a , tells us that not very much of the original acid ionizes. Thus we can assume that $x \ll 0.10$. If x is small enough compared with 0.10, it will not matter (much) whether we subtract it, and we can assume that $(0.10 - x)$ is very nearly equal to 0.10. The equation then becomes

$$\frac{x^2}{0.10} \approx 3.5 \times 10^{-8} \quad x^2 \approx 3.5 \times 10^{-9} \quad \text{so} \quad x \approx 5.9 \times 10^{-5}$$

In our algebraic representation we let

$$[\text{H}_3\text{O}^+] = x M = 5.9 \times 10^{-5} M; [\text{OCl}^-] = x M = 5.9 \times 10^{-5} M$$

$$[\text{HOCl}] = (0.10 - x) M = (0.10 - 0.000059) M = 0.10 M$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-5}} = 1.7 \times 10^{-10} M$$

$$\text{(b) pH} = -\log(5.9 \times 10^{-5}) = 4.23$$

You should now work Exercise 42.

STOP & THINK

We neglect the $1.0 \times 10^{-7} \text{ mol/L}$ of H_3O^+ produced by the ionization of pure water. Recall (Section 18-2) that the addition of an acid to water suppresses the ionization of H_2O , so $[\text{H}_3\text{O}^+]$ from H_2O is even less than $1.0 \times 10^{-7} M$.

STOP & THINK

Because $x \approx 5.9 \times 10^{-5}$, it is more than two orders of magnitude smaller than 0.10. Thus our approximation of neglecting x in the expression $0.10 - x$ to simplify the algebra was a good one.

Problem-Solving Tip Simplifying Quadratic Equations

We often encounter quadratic or higher-order equations in equilibrium calculations. With modern programmable calculators, solving such problems by iterative methods is often feasible. But frequently a problem can be made much simpler by using some mathematical common sense.

When the linear variable (x) in a *quadratic* equation is added to or subtracted from a much larger number, it can often be disregarded if it is sufficiently small. A reasonable rule of thumb for determining whether the variable can be disregarded in equilibrium calculations is this: If the exponent of 10 in the K value is -3 (e.g., 10^{-3}) or less (-4 , -5 , -6 , etc.), then the variable may be small enough to disregard when it is added to or subtracted from a number two orders of magnitude greater (e.g., 0.1 if $K_a = 0.001$ or 1×10^{-3}). Solve the problem neglecting x ; then compare the value of x with the number it would have been added to (or subtracted from). If x is more than 5% of that number, the assumption was *not* justified, and you should solve the equation using the quadratic formula.



The pH of a Diet Coke is measured with a modern pH meter. Many carbonated soft drinks are acidic due to the dissolved CO_2 and phosphoric acid (both weak acids).

Let's examine the assumption as it applies to Example 18-10. Our quadratic equation is

$$\frac{(x)(x)}{(0.10 - x)} = 3.5 \times 10^{-8}$$

Because 3.5×10^{-8} is a very small K_a value, we know that the acid ionizes only slightly. Thus, x must be very small compared with 0.10, so we can write $(0.10 - x) \approx 0.10$.

The equation then becomes $\frac{x^2}{0.10} \approx 3.5 \times 10^{-8}$. To solve this, we rearrange and take the square roots of both sides. To check, we see that the result, $x \approx 5.9 \times 10^{-5}$, is only 0.059% of 0.10. This error is much less than 5%, so our assumption is justified. You may also wish to use the quadratic formula to verify that the answer obtained this way is correct to within roundoff error.

The preceding argument is purely algebraic. We could use our chemical intuition to reach the same conclusion. A small K_a value (10^{-3} or less) tells us that the extent of ionization is very small; therefore, nearly all of the weak acid exists as nonionized molecules. The amount that ionizes is insignificant compared with the concentration of nonionized weak acid.

From our calculations in Example 18-10, we can draw some conclusions. In a solution containing *only a weak monoprotic acid*, the concentration of H_3O^+ is equal to the concentration of the anion of the acid. The concentration of the dilute nonionized acid is approximately equal to the molarity of the solution.

EXAMPLE 18-11 Percent Ionization

Calculate the percent ionization of a 0.10 M solution of acetic acid.

Plan

Write the ionization equation and the expression for K_a . Follow the procedure used in Example 18-10 to find the concentration of acid that ionized. Then, substitute the concentration of acid that ionized into the expression for percent ionization. Percentage is defined as (part/whole) $\times 100\%$, so the percent ionization is

$$\% \text{ ionization} = \frac{[\text{CH}_3\text{COOH}]_{\text{ionized}}}{[\text{CH}_3\text{COOH}]_{\text{initial}}} \times 100\%$$

Solution

The equations for the ionization of CH_3COOH and its K_a are



We proceed as we did in Example 18-10. Let $x = [\text{CH}_3\text{COOH}]_{\text{ionized}}$.



initial	0.10 M	$\approx 0 \text{ M}$	0 M
change due to rxn	$-x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
at equil	$(0.10 - x) \text{ M}$	$x \text{ M}$	$x \text{ M}$

Substituting into the ionization constant expression gives

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(x)}{(0.10 - x)} = 1.8 \times 10^{-5}$$

If we make the simplifying assumption that $(0.10 - x) \approx 0.10$, we have

$$\frac{x^2}{0.10} = 1.8 \times 10^{-5} \quad x^2 = 1.8 \times 10^{-6} \quad x = 1.3 \times 10^{-3}$$

► We could write the initial $[\text{H}_3\text{O}^+]$ as $1.0 \times 10^{-7} \text{ M}$. In very *dilute* solutions of weak acids, we might have to take this into account. In this acid solution, $(1.0 \times 10^{-7} + x) \approx x$.

This gives $[\text{CH}_3\text{COOH}]_{\text{ionized}} = x = 1.3 \times 10^{-3} \text{ M}$. Now we can calculate the percent ionization for $0.10 \text{ M CH}_3\text{COOH}$ solution.

$$\% \text{ ionization} = \frac{[\text{CH}_3\text{COOH}]_{\text{ionized}}}{[\text{CH}_3\text{COOH}]_{\text{initial}}} \times 100\% = \frac{1.3 \times 10^{-3} \text{ M}}{0.10 \text{ M}} \times 100\% = 1.3\%$$

Our assumption that $(0.10 - x) \approx 0.10$ is reasonable because $(0.10 - x) = (0.10 - 0.0013)$. Thus, x is approximately two orders of magnitude smaller than the 0.10 value it is being subtracted from (or only about 1% different than 0.10). When K_a for a weak acid is significantly greater than 10^{-3} , however, this assumption would introduce considerable error because the x value would be large enough to cause a significant change when subtracted from the initial concentration.

You should now work Exercise 48.

In dilute solutions, acetic acid exists primarily as nonionized molecules, as do all weak acids; there are relatively few hydronium and acetate ions. In 0.10 M solution, CH_3COOH is 1.3% ionized; for each 1000 molecules of CH_3COOH originally placed in the solution, there are 13 H_3O^+ ions, 13 CH_3COO^- ions, and 987 nonionized CH_3COOH molecules. For weaker acids of the same concentration, the number of molecules of nonionized acid would be even larger.

By now we should have gained some “feel” for the strength of an acid by looking at its K_a value. Consider 0.10 M solutions of HCl (a strong acid), CH_3COOH (Example 18-11), and HOCl (Example 18-10). If we calculate the percent ionization for 0.10 M HOCl (as we did for $0.10 \text{ M CH}_3\text{COOH}$ in Example 18-11), we find that it is 0.059% ionized. In 0.10 M solution, HCl is very nearly completely ionized (100%). The data in Table 18-5 show that the $[\text{H}_3\text{O}^+]$ in 0.10 M HCl is approximately 77 times greater than that in $0.10 \text{ M CH}_3\text{COOH}$ and approximately 1700 times greater than that in 0.10 M HOCl .

Many scientists prefer to use $\text{p}K_a$ values rather than K_a values for weak acids. Recall that in general, “p” terms refer to negative logarithms. The $\text{p}K_a$ value for a weak acid is just the negative logarithm of its K_a value.

$$\text{p}K_a = -\log K_a$$

EXAMPLE 18-12 $\text{p}K_a$ Values

The K_a values for acetic acid and hydrofluoric acid are 1.8×10^{-5} and 7.2×10^{-4} , respectively. What are their $\text{p}K_a$ values?

Plan

$\text{p}K_a$ is defined as the negative logarithm of K_a , so we take the negative logarithm of each K_a .

Solution

For CH_3COOH ,

$$\text{p}K_a = -\log K_a = -\log (1.8 \times 10^{-5}) = -(-4.74) = 4.74$$

For HF ,

$$\text{p}K_a = -\log K_a = -\log (7.2 \times 10^{-4}) = -(-3.14) = 3.14$$

You should now work Exercise 50.

Table 18-5 Comparison of Extents of Ionization of Some Acids

Acid Solution	Ionization Constant	$\text{p}K_a$	$[\text{H}_3\text{O}^+]$	pH	Percent Ionization
0.10 M HCl	very large	—	0.10 M	1.00	≈ 100
$0.10 \text{ M CH}_3\text{COOH}$	1.8×10^{-5}	4.74	0.0013 M	2.89	1.3
0.10 M HOCl	3.5×10^{-8}	7.46	0.000059 M	4.23	0.059

► Note that we did not need to solve explicitly for the equilibrium concentrations $[\text{H}_3\text{O}^+]$ and $[\text{CH}_3\text{COO}^-]$ to answer the question. From the setup, we see that these are both $1.3 \times 10^{-3} \text{ M}$.



An inert solid has been suspended in the liquid to improve the quality of this photograph of a pH meter.

Unless otherwise noted, all content on this page is © Cengage Learning.

From Example 18-12, we see that the stronger acid (HF in this case) has the larger K_a value and the smaller pK_a value. Conversely, the weaker acid (CH_3COOH in this case) has the smaller K_a value and the larger pK_a value.

► A similar statement is true for weak bases; that is, a stronger base has the greater K_b value and the smaller pK_b value.

The weaker an acid, the smaller its value of K_a , and the larger its value of pK_a .

Similarly, the weaker a base, the smaller its value of K_b and the larger its value of pK_b .

Strong acids have large K_a values and *negative* pK_a values. HCl, for example, has a $K_a \approx 1 \times 10^8$ and a $pK_a \approx -8$.

EXAMPLE 18-13 Acid Strengths and K_a Values

Given the following list of weak acids and their K_a values, arrange the acids in order of (a) increasing acid strength and (b) increasing pK_a values.

Acid	K_a
HOCl	3.5×10^{-8}
HCN	4.0×10^{-10}
HNO_2	4.5×10^{-4}

Plan

(a) We see that HNO_2 is the strongest acid in this group because it has the largest K_a value. HCN is the weakest because it has the smallest K_a value. (b) We do not need to calculate pK_a values to answer the question. We recall that the weakest acid has the largest pK_a value and the strongest acid has the smallest pK_a value, so the order of increasing pK_a values is just the reverse of the order in Part (a).

Solution

- (a) Increasing acid strength: $\text{HCN} < \text{HOCl} < \text{HNO}_2$
 (b) Increasing pK_a values: $\text{HNO}_2 < \text{HOCl} < \text{HCN}$

You should now work Exercise 109.

Weakest to strongest acids:

Acid	K_a	pK_a
HCN	4.0×10^{-10}	9.40
HOCl	3.5×10^{-8}	7.46
HNO_2	4.5×10^{-4}	3.35

Increasing acidity
↓

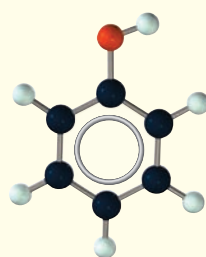
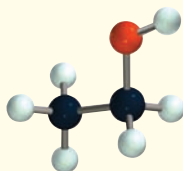
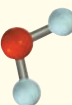
► Do not confuse the strength of an acid with its reactivity. Acid strength refers to the extent of ionization of the acid and not to the reactions that it undergoes.

You may know that hydrofluoric acid dissolves glass. But HF is *not* a strong acid. The reaction of glass with hydrofluoric acid occurs because silicates react with HF to produce silicon tetrafluoride, SiF_4 , or $[\text{SiF}_6]^{2-}$ in aqueous solution. This reaction tells us nothing about the acid strength of hydrofluoric acid, just that it has unusual reactivity towards SiO_2 (glass).

In Chapter 10 we studied the strengths of binary acids as a function of the position of the anion on the periodic table. We also studied the strengths of ternary acids containing the same central element as a function of the oxidation state of the central element. Those were empirical trends. We can now use K_a and pK_a values to make much more precise conclusions about compounds' acidity or basicity. The following example illustrates a correlation between K_a values and properties.

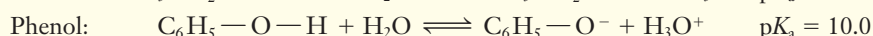
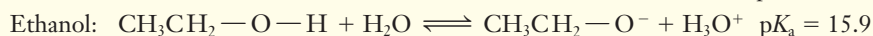
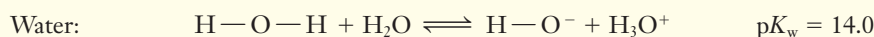
EXAMPLE 18-14 Comparison of the Acid Strength of Classes of Compounds

The structures of phenol, the smallest member of the group of compounds called phenols ($\text{C}_6\text{H}_5\text{OH}$), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and water (HOH) are shown here.

Phenol, C₆H₅OHEthanol, C₂H₅OHWater, H₂O

► The circle in the phenol ring indicates delocalized π -bonding.

We see that each contains an —O—H group, which can undergo an acid reaction. These three reactions and their $\text{p}K_{\text{a}}$ values are



(a) Rank the three compounds in order of decreasing acidity. (b) Calculate the pH of 0.010 *M* solutions of ethanol and phenol and compare them to the acidity of pure water.

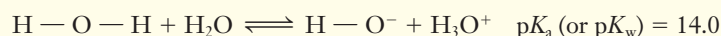
Plan

(a) Knowing the acidity, $\text{p}K_{\text{a}}$, of each compound, we can rank the compounds according to acidity. (b) From the equations for the ionization of each compound acting as an acid, we can write each K_{a} expression and substitute into it. Then we solve the resulting expression for the concentration of hydronium ion and determine the pH.

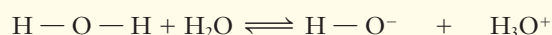
Solution

- (a) Phenol has the lowest value for $\text{p}K_{\text{a}}$, so it is the strongest acid. Water is the next strongest acid of these three compounds. Ethanol has the largest $\text{p}K_{\text{a}}$, and, therefore, is the weakest acid.

- (b) *For water:*



$$\text{Therefore, } K_{\text{a}} = 1.0 \times 10^{-14}$$



Due to autoionization

$$1.0 \times 10^{-7} \text{ M} \quad 1.0 \times 10^{-7} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 1 \times 10^{-7} \quad \text{pH} = 7.00$$

For phenol:



initial	0.010 <i>M</i>	0 <i>M</i>	$1.0 \times 10^{-7} \text{ M}$
change due to ionization	$-x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
at equil	$(0.010 - x) \text{ M}$	$x \text{ M}$	$x + (1.0 \times 10^{-7}) \text{ M}$

$$\text{p}K_{\text{a}} = 10.0; \text{ therefore, } K_{\text{a}} = 1.0 \times 10^{-10}$$

Substituting into the ionization constant expression gives

$$1.0 \times 10^{-10} = \frac{x(x + (1.0 \times 10^{-7}))}{0.010 - x}$$

If we make the usual assumptions that $(0.010 - x) \approx 0.010 \text{ M}$ and that $x + (1.0 \times 10^{-7}) \approx x \text{ M}$, we have

$$1.0 \times 10^{-10} = \frac{x^2}{0.010} \quad x^2 = 1.0 \times 10^{-12} \quad x = 1.0 \times 10^{-6} \text{ M}$$

This gives $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-6} \quad \text{pH} = 6.00$

[Solving by use of the quadratic formula yields $[\text{H}_3\text{O}^+] = 1.1 \times 10^{-6} \text{ M}$ or $\text{pH} = 5.96$]

► The lower the $\text{p}K_{\text{a}}$ is, the larger the K_{a} and the stronger the compound when acting as an acid.

STOP & THINK

It is not always x that is small enough to neglect! In the numerator, the number 1.0×10^{-7} is negligible compared to the variable x .

For ethanol:

$\text{CH}_3\text{CH}_2\text{O} - \text{H} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O}^- + \text{H}_3\text{O}^+ \quad \text{p}K_a = 15.9 \quad K_a = 1.26 \times 10^{-16}$			
$\text{CH}_3\text{CH}_2\text{O} - \text{H} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O}^- + \text{H}_3\text{O}^+$			
initial	0.010 M	0 M	$1.0 \times 10^{-7} \text{ M}$
change due to ionization	$-x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
at equil	$(0.010 - x) \text{ M}$	$x \text{ M}$	$x + (1.0 \times 10^{-7}) \text{ M}$

We can make the usual assumption that $(0.010 - x) \approx 0.010 \text{ M}$, but the usual assumption that $x + (1.0 \times 10^{-7}) \approx x \text{ M}$ will not be correct in this case. You can prove this by assuming that $x + (1.0 \times 10^{-7}) \approx x \text{ M}$ and solving for x . You will obtain $[\text{H}_3\text{O}^+] = 1 \times 10^{-9} \text{ M}$. For very weak and very dilute acids (or bases), the quantity of hydrogen ion (or hydroxide ion) produced will be small compared to the quantity produced by the solvent, water. For very weak acids, the $[\text{H}_3\text{O}^+]$ at equilibrium can be considered to be that formed by pure water, $1.0 \times 10^{-7} \text{ M}$, with a negligible amount added by the ionization of the ethanol. The acceptable assumption would be that

$$x + (1.0 \times 10^{-7}) \approx 1.0 \times 10^{-7} \text{ M}$$

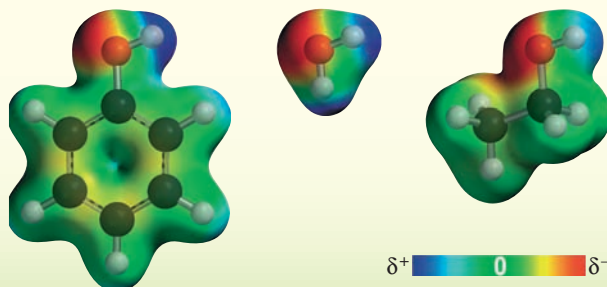
$$K_a = 1.26 \times 10^{-16} = \frac{x(1.0 \times 10^{-7})}{0.010} \quad x = 1.26 \times 10^{-11}$$

Substituting into the concentration values, we obtain

$$[\text{H}_3\text{O}^+] = (1.26 \times 10^{-11}) + (1.0 \times 10^{-7}) = 1.0 \times 10^{-7} \quad \text{pH} = 7.00$$

We see that phenol, which is a stronger acid than water, results in an aqueous solution that has a pH less than 7 (an acidic solution). However, ethanol, which is a weaker acid than water, results in an aqueous solution that has the same acidity as pure water (pH = 7.0).

► The acidity of a molecule depends not just on the polarity of the O—H bond as shown by the greater δ^- and δ^+ charge differential (red-blue color intensity) in the electrostatic charge potential plots, but also on the stabilization of the conjugate base (anion) after dissociation of the H^+ . Phenol can stabilize its anion more effectively than ethanol due to the delocalized π -bonding in the C_6 ring system.



You should now work Exercises 32 and 33.

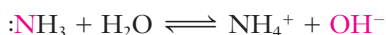


Ammonia, NH_3

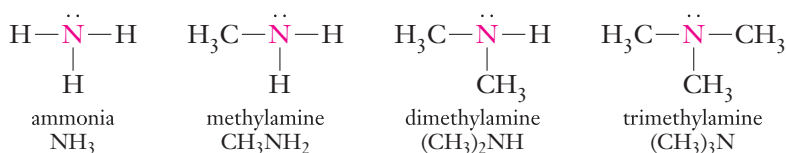


Trimethylamine, $(\text{CH}_3)_3\text{N}$

Thus far we have focused our attention on acids. Very few common weak bases are soluble in water. Aqueous ammonia is the most frequently encountered example. From our earlier discussion of bonding in covalent compounds (see Section 8-8), we recall that there is one lone pair of electrons on the nitrogen atom in NH_3 . When ammonia dissolves in water, it accepts H^+ from a water molecule in a reversible reaction (see Section 10-4). We say that NH_3 ionizes slightly when it undergoes this reaction. Aqueous solutions of NH_3 are basic because OH^- ions are produced.

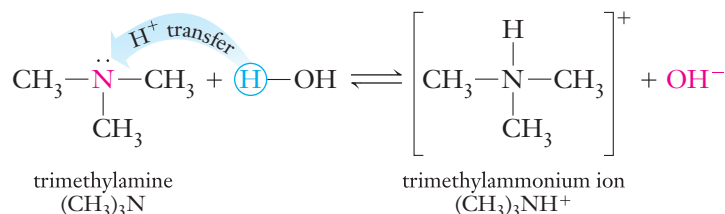


Amines are derivatives of NH_3 in which one or more H atoms have been replaced by organic groups, as the following structures indicate.

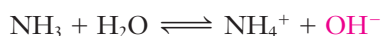


The nitrogen atom becomes increasingly basic with the addition of hydrocarbon groups such as CH_3 (methyl). These are considered electron-donating and increase the δ^- charge on the nitrogen and the ability of the lone pair of electrons to remove H^+ from water.

Thousands of amines are known, and many are very important in biochemical processes. Low-molecular-weight amines are soluble weak bases. The ionization of trimethylamine, for example, forms trimethylammonium ions and OH^- ions.



Now let us consider the behavior of ammonia in aqueous solutions. The reaction of ammonia with water and its ionization constant expression are



and

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

The fact that K_b for aqueous NH_3 has the same value as K_a for CH_3COOH is just a coincidence. It does tell us that in aqueous solutions of the same concentration, CH_3COOH and NH_3 are ionized to the same extent. Table 18-6 lists K_b and $\text{p}K_b$ values for a few common weak bases. Appendix G includes a longer list of K_b values.

We use K_b and $\text{p}K_b$ values for weak bases in the same way we used K_a and $\text{p}K_a$ values for weak acids.

Table 18-6 Ionization Constants and $\text{p}K_b$ Values for Some Weak Bases

Base	Ionization Reaction	K_b at 25°C	$\text{p}K_b$
ammonia	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	1.8×10^{-5}	4.74
methylamine	$(\text{CH}_3)\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)\text{NH}_3^+ + \text{OH}^-$	5.0×10^{-4}	3.30
dimethylamine	$(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+ + \text{OH}^-$	7.4×10^{-4}	3.13
trimethylamine	$(\text{CH}_3)_3\text{N} + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+ + \text{OH}^-$	7.4×10^{-5}	4.13
pyridine	$\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+ + \text{OH}^-$	1.5×10^{-9}	8.82
aniline	$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	4.2×10^{-10}	9.38

EXAMPLE 18-15 pH of a Weak Base Solution

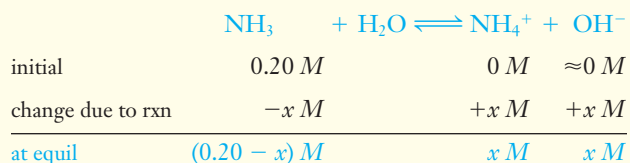
Calculate the $[\text{OH}^-]$, pH, and percent ionization for a 0.20 M aqueous NH_3 solution.

Plan

Write the equation for the ionization of aqueous NH_3 and represent the equilibrium concentrations algebraically. Then substitute into the K_b expression and solve for $[\text{OH}^-]$ and $[\text{NH}_3]_{\text{ionized}}$. Knowing $[\text{OH}^-]$, we calculate pOH, and from that we can find pH.

Solution

The equation for the ionization of aqueous ammonia and the algebraic representations of equilibrium concentrations follow. Let $x = [\text{NH}_3]_{\text{ionized}}$.

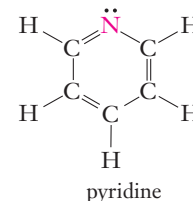
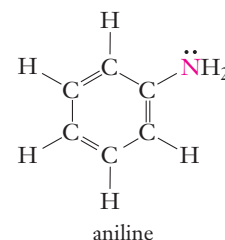


Charles D. Winters

The odor that we associate with fish is due to the presence of amines. This is one reason why lemon is often added to seafood. The citric acid (a weak acid) neutralizes the odor of the amines.

► The subscript “b” in K_b and $\text{p}K_b$ indicates that the substance ionizes as a base. We do not include $[\text{H}_2\text{O}]$ in the K_b expression for the same reasons described for K_a .

$$\text{p}K_b = -\log K_b$$



► Since K_a and K_b values are usually known to only two significant figures, many answers in the following calculations will be limited to two significant figures. pH = 11.28, for example, has only two significant figures because the 11 relates to the exponent of ten.

► The value of x is only about 1% of the original concentration, so the assumption is justified.

Substitution into the ionization constant expression gives

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.20 - x)}$$

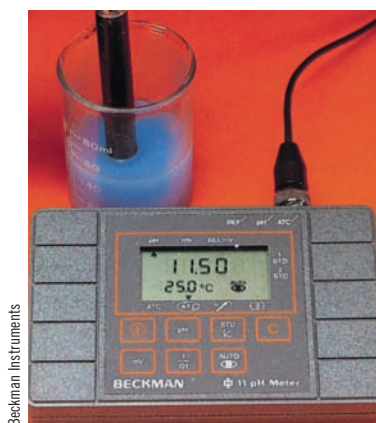
Again, we can simplify this equation. The small value of K_b tells us that the base is only slightly ionized, so we can assume that $x \ll 0.20$, or $(0.20 - x) \approx 0.20$, and we have

$$\frac{x^2}{0.20} = 1.8 \times 10^{-5} \quad x^2 = 3.6 \times 10^{-6} \quad x = 1.9 \times 10^{-3} M$$

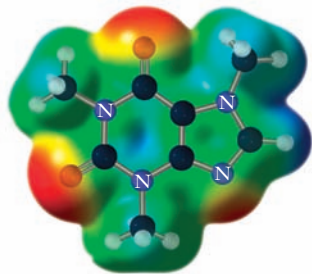
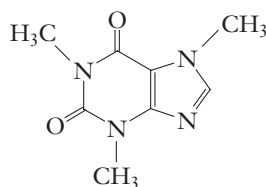
Then $[\text{OH}^-] = x = 1.9 \times 10^{-3} M$, $\text{pOH} = 2.72$, and $\text{pH} = 14 - \text{pOH} = 11.28$. $[\text{NH}_3]_{\text{ionized}} = x$, so the percent ionization may be calculated.

$$\% \text{ ionization} = \frac{[\text{NH}_3]_{\text{ionized}}}{[\text{NH}_3]_{\text{initial}}} \times 100\% = \frac{1.9 \times 10^{-3}}{0.20} \times 100\% = 0.95\% \text{ ionized}$$

You should now work Exercises 54 and 108.



Measurement of the pH of a solution of household ammonia.



Caffeine is an example of a weak base.

EXAMPLE 18-16 Household Ammonia

The pH of a household ammonia solution is 11.50. What is its molarity? Assume that ammonia is the only base (or acid) present.

Plan

We are given the pH of an aqueous NH_3 solution. Use $\text{pH} + \text{pOH} = 14.00$ to find pOH , which we can convert to $[\text{OH}^-]$. Then complete the ionization reaction summary, and substitute the representations of equilibrium concentrations into the K_b expression.

Solution

At equilibrium pH = 11.50; we know that $\text{pOH} = 2.50$, so $[\text{OH}^-] = 10^{-2.50} = 3.2 \times 10^{-3} M$. This $[\text{OH}^-]$ results from the reaction, so we can write the change line. Then, letting x represent the *initial* concentration of NH_3 , we can complete the reaction summary.

At equilibrium $[\text{OH}^-] = 3.2 \times 10^{-3} M$, so

	NH_3	+	H_2O	$\rightleftharpoons$	NH_4^+	+	OH^-	
Initial	$x M$				$0 M$		$\approx 0 M$	
change	$-3.2 \times 10^{-3} M$				$+3.2 \times 10^{-3} M$		$+3.2 \times 10^{-3} M$	
at equil	$(x - 3.2 \times 10^{-3}) M$				$3.2 \times 10^{-3} M$		$3.2 \times 10^{-3} M$	

Substituting these values into the K_b expression for aqueous NH_3 gives

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(3.2 \times 10^{-3})(3.2 \times 10^{-3})}{(x - 3.2 \times 10^{-3})} = 1.8 \times 10^{-5}$$

This suggests that $(x - 3.2 \times 10^{-3}) \approx x$. So we can approximate.

$$\frac{(3.2 \times 10^{-3})(3.2 \times 10^{-3})}{x} = 1.8 \times 10^{-5} \quad \text{and} \quad x = 0.57 M \text{ NH}_3$$

The solution is $0.57 M \text{ NH}_3$. Our assumption that $(x - 3.2 \times 10^{-3}) \approx x$ is justified.

You should now work Exercises 32, 54, and 56.



Problem-Solving Tip It Is Not Always x That Can Be Neglected

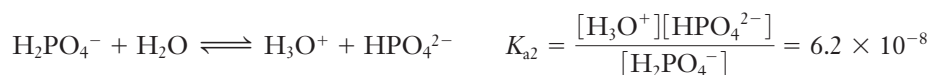
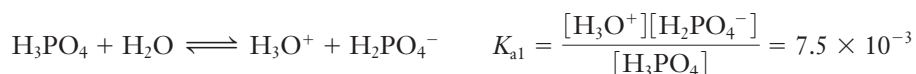
Students sometimes wonder about the approximation in Example 18-16, thinking that only x can be neglected. We can consider neglecting one term in an expression only when the expression involves *addition* or *subtraction*. The judgment we must make is whether *either* of the terms is sufficiently smaller than the other that ignoring it would not significantly affect the result. In Example 18-16, x represents the *initial* concentration of NH_3 ; 3.2×10^{-3} represents the concentration that ionizes, which cannot be greater than the original x . We know that NH_3 is a *weak* base ($K_b = 1.8 \times 10^{-5}$), so only a small amount of the original ionizes. We can safely assume that $3.2 \times 10^{-3} \ll x$, so $(x - 3.2 \times 10^{-3}) \approx x$, the approximation that we used in solving the example.

STOP & THINK

We can *never* neglect any term in multiplication or division!

18-5 Polyprotic Acids

Thus far we have considered only *monoprotic* weak acids. Acids that can furnish *two* or more hydronium ions per molecule are called **polyprotic acids**. The ionizations of polyprotic acids occur stepwise, that is, one proton at a time. An ionization constant expression can be written for each step, as the following example illustrates. Consider phosphoric acid as a typical polyprotic acid. It contains three acidic hydrogen atoms and ionizes in three steps.



We see that K_{a1} is much greater than K_{a2} , and that K_{a2} is much greater than K_{a3} . This is generally true for polyprotic *inorganic* acids (Appendix F). Successive ionization constants often decrease by a factor of approximately 10^4 to 10^6 , although some differences are outside this range. Large decreases in the values of successive ionization constants mean that each step in the ionization of a polyprotic acid occurs to a much lesser extent than the previous step. Thus, the $[\text{H}_3\text{O}^+]$ produced in the first step is very large compared with the $[\text{H}_3\text{O}^+]$ produced in the second and third steps. As we shall see, except in extremely dilute solutions of H_3PO_4 , the concentration of H_3O^+ may be assumed to be that furnished by the first step in the ionization alone.

EXAMPLE 18-17 Solution of a Weak Polyprotic Acid

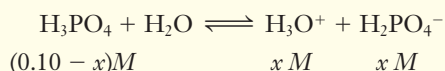
Calculate the concentrations of all species present in 0.10 M H_3PO_4 .

Plan

Because H_3PO_4 contains three acidic hydrogens per formula unit, we show its ionization in three steps. For each step, write the appropriate ionization equation, with its K_a expression and value. Then represent the equilibrium concentrations from the *first* ionization step, and substitute into the K_{a1} expression. Repeat the procedure for the second and third steps *in order*.

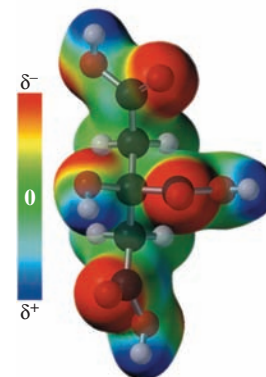
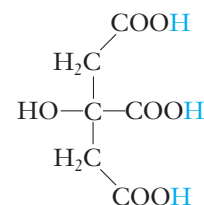
Solution

First we calculate the concentrations of all species that are formed in the first ionization step. Let $x = \text{mol/L}$ of H_3PO_4 that ionize; then $x = [\text{H}_3\text{O}^+]_{1\text{st}} = [\text{H}_2\text{PO}_4^-]$.



► Each K_a expression includes $[\text{H}_3\text{O}^+]$, so each K_a expression must be satisfied by the total concentration of H_3O^+ in the solution.

► Citrus fruits contain citric acid and ascorbic acid (vitamin C). Citric acid is an example of an organic triprotic weak acid. The structure of citric acid is:



Substitution into the expression for K_{a1} gives

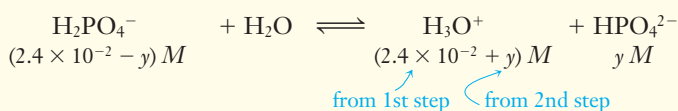
$$K_{a1} = \frac{[\text{H}_3\text{O}^+]_{1\text{st}}[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3} = \frac{(x)(x)}{(0.10 - x)}$$

► $x = -3.1 \times 10^{-2}$ is the extraneous root of the quadratic formula.

This equation must be solved by the quadratic formula because K_{a1} is too large to neglect x relative to 0.10 M . Solving gives the *positive* root $x = 2.4 \times 10^{-2}$. Thus, from the first step in the ionization of H_3PO_4 ,

$$\begin{aligned} x\text{ M} &= [\text{H}_3\text{O}^+]_{1\text{st}} = [\text{H}_2\text{PO}_4^-] = 2.4 \times 10^{-2}\text{ M} \\ (0.10 - x)\text{ M} &= [\text{H}_3\text{PO}_4] = 7.6 \times 10^{-2}\text{ M} \end{aligned}$$

For the second step, we use the $[\text{H}_3\text{O}^+]$ and $[\text{H}_2\text{PO}_4^-]$ from the first step. Let $y = \text{mol/L}$ of $\text{H}_2\text{PO}_4^{2-}$ that ionize; then $y = [\text{H}_3\text{O}^+]_{2\text{nd}} = [\text{HPO}_4^{2-}]$.



Substitution into the expression for K_{a2} gives

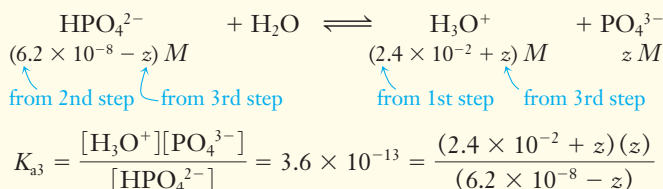
$$K_{a2} = \frac{[\text{H}_3\text{O}^+]_{1\text{st} \& 2\text{nd}}[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.2 \times 10^{-8} = \frac{(2.4 \times 10^{-2} + y)(y)}{(2.4 \times 10^{-2} - y)}$$

Examination of this equation suggests that $y \ll 2.4 \times 10^{-2}$, so

$$\frac{(2.4 \times 10^{-2})(y)}{2.4 \times 10^{-2}} = 6.2 \times 10^{-8} \quad y = 6.2 \times 10^{-8}\text{ M} = [\text{HPO}_4^{2-}] = [\text{H}_3\text{O}^+]_{2\text{nd}}$$

We see that $[\text{HPO}_4^{2-}] = K_{a2}$ and $[\text{H}_3\text{O}^+]_{2\text{nd}} \ll [\text{H}_3\text{O}^+]_{1\text{st}}$. In general, in solutions of reasonable concentration of weak polyprotic acids for which $K_{a1} \gg K_{a2}$ and that contain no other electrolytes, *the concentration of the anion produced in the second ionization step is always equal to K_{a2} .*

For the third step, we use $[\text{H}_3\text{O}^+]$ from the *first* step and $[\text{HPO}_4^{2-}]$ from the *second* step. Let $z = \text{mol/L}$ of HPO_4^{2-} that ionize; then $z = [\text{H}_3\text{O}^+]_{3\text{rd}} = [\text{PO}_4^{3-}]$.



We make the usual simplifying assumption, and find that

$$z\text{ M} = 9.3 \times 10^{-19}\text{ M} = [\text{PO}_4^{3-}] = [\text{H}_3\text{O}^+]_{3\text{rd}}$$

The $[\text{H}_3\text{O}^+]$ found in the three steps can be summarized:

$$\begin{array}{rcl} [\text{H}_3\text{O}^+]_{1\text{st}} & = & 2.4 \times 10^{-2}\text{ M} = 0.024\text{ M} \\ [\text{H}_3\text{O}^+]_{2\text{nd}} & = & 6.2 \times 10^{-8}\text{ M} = 0.000000062\text{ M} \\ [\text{H}_3\text{O}^+]_{3\text{rd}} & = & 9.3 \times 10^{-19}\text{ M} = 0.0000000000000000093\text{ M} \\ \hline [\text{H}_3\text{O}^+]_{\text{total}} & = & 2.4 \times 10^{-2}\text{ M} = 0.024\text{ M} \end{array}$$

We see that the H_3O^+ furnished by the second and third steps of ionization is negligible compared with that from the first step.

You should now work Exercise 58.

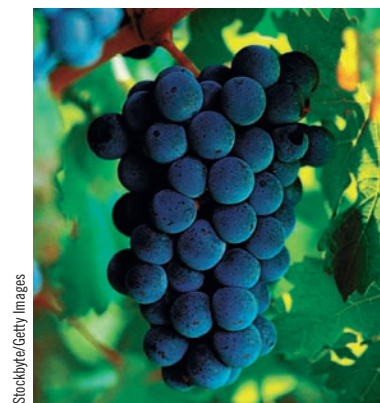
We have calculated the concentrations of the species formed by the ionization of 0.10 M H_3PO_4 . These concentrations are compared in Table 18-7. The concentration of $[\text{OH}^-]$ in 0.10 M H_3PO_4 is included. It was calculated from the known $[\text{H}_3\text{O}^+]$ using the ion product for water, $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$.

Table 18-7 Concentrations of the Species in 0.100 M H₃PO₄ (Example 18-17)

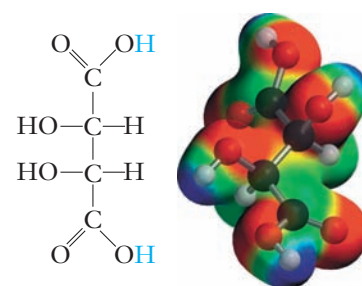
Species	Concentration (mol/L)
H ₃ PO ₄	$7.6 \times 10^{-2} = 0.076$
H ₃ O ⁺	$2.4 \times 10^{-2} = 0.024$
H ₂ PO ₄ ⁻	$2.4 \times 10^{-2} = 0.024$
HPO ₄ ²⁻	$6.2 \times 10^{-8} = 0.000000062$
OH ⁻	$4.2 \times 10^{-13} = 0.00000000000042$
PO ₄ ³⁻	$9.3 \times 10^{-19} = 0.0000000000000000093$

Nonionized H₃PO₄ is present in greater concentration than any other species in 0.10 M H₃PO₄ solution. The only other species present in significant concentrations are H₃O⁺ and H₂PO₄⁻. Similar statements can be made for other weak polyprotic acids for which the last *K* is very small.

Phosphoric acid is a typical *weak* polyprotic acid. Let us now describe solutions of sulfuric acid, a *very strong* polyprotic acid.



Stockbyte/Getty Images



Tartaric acid is an example of a weak polyprotic acid. It contains two acidic protons. Tartaric acid and its salts are found in grapes.

EXAMPLE 18-18 Solution of a Strong Polyprotic Acid

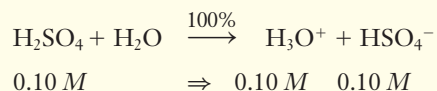
Calculate concentrations of all species present in 0.10 M H₂SO₄. $K_{a2} = 1.2 \times 10^{-2}$.

Plan

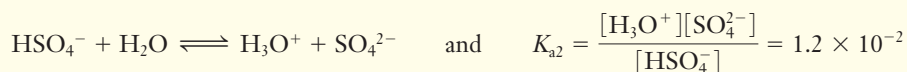
Because the first ionization step of H₂SO₄ is complete, we read the concentrations for the first step from the balanced equation. The second ionization step is not complete, so we write the ionization equation, the K_{a2} expression, and the algebraic representations of equilibrium concentrations. Then we substitute into K_{a2} for H₂SO₄.

Solution

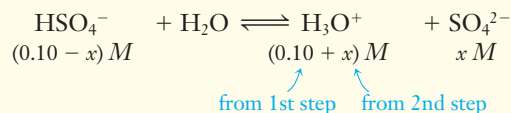
As we pointed out, the first ionization step of H₂SO₄ is complete.



The second ionization step is not complete, however.



Let $x = [\text{HSO}_4^-]$ that ionizes. $[\text{H}_3\text{O}^+]$ is the sum of the concentrations produced in the first and second steps. So we represent the equilibrium concentrations as



Substitution into the ionization constant expression for K_{a2} gives

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = 1.2 \times 10^{-2} = \frac{(0.10 + x)(x)}{0.10 - x}$$

► The pH of solutions of most polyprotic acids is governed by the first ionization step.

A pH of 0.10 M H₃PO₄B pH of 0.10 M H₂SO₄

pH comparison for equimolar solutions of two polyprotic acids.

Clearly, x cannot be disregarded because K_{a2} is too large. This equation must be solved by the quadratic formula, which gives $x = 0.010$ and $x = -0.12$ (extraneous). So $[\text{H}_3\text{O}^+]_{2\text{nd}} = [\text{SO}_4^{2-}] = 0.010 M$. The concentrations of species in 0.10 M H₂SO₄ are

$$\begin{aligned} [\text{H}_2\text{SO}_4] &\approx 0 M ; [\text{HSO}_4^-] = (0.10 - x) M = 0.09 M ; [\text{SO}_4^{2-}] = 0.010 M \\ [\text{H}_3\text{O}^+] &= (0.10 + x) M = 0.11 M \\ [\text{OH}^-] &= \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{0.11} = 9.1 \times 10^{-14} M \end{aligned}$$

In 0.10 M H₂SO₄ solution, the extent of the second ionization step is 10%.

You should now work Exercise 60.

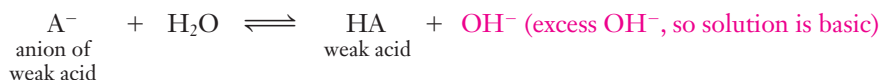
In Table 18-8 we compare 0.10 M solutions of these two polyprotic acids. Their acidities are very different.

Table 18-8 Comparison of 0.10 M Solutions of Two Polyprotic Acids (Examples 18-17, 18-18)

	0.10 M H ₃ PO ₄	0.10 M H ₂ SO ₄
K_{a1}	7.5×10^{-3}	very large
K_{a2}	6.2×10^{-8}	1.2×10^{-2}
K_{a3}	3.6×10^{-13}	—
$[\text{H}_3\text{O}^+]$	$2.4 \times 10^{-2} M$	0.11 M
pH	1.62	0.96
[nonionized molecules]	$7.6 \times 10^{-2} M$	$\approx 0 M$

18-6 Solvolysis

Solvolysis is the reaction of a substance with the solvent in which it is dissolved. The solvolysis reactions that we will consider in this chapter occur in aqueous solutions, so they are called *hydrolysis* reactions. **Hydrolysis** is the reaction of a substance with water. Some hydrolysis reactions involve reaction with H_3O^+ or OH^- ions. One common kind of hydrolysis involves reaction of the anion of a *weak acid* (the conjugate base) with water to form *nonionized acid* molecules and OH^- ions. This upsets the $\text{H}_3\text{O}^+/\text{OH}^-$ balance in water and produces basic solutions. This reaction is usually represented as



Recall that in

basic solutions $[\text{H}_3\text{O}^+] < [\text{OH}^-]$ or $[\text{OH}^-] > 1.0 \times 10^{-7} M$

neutral solutions $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} M$

acidic solutions $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ or $[\text{H}_3\text{O}^+] > 1.0 \times 10^{-7} M$

► Examples of conjugate acid–base pairs.

Acid → **Conjugate Base**
 strong (HCl) → very weak (Cl^-)
 weak (HCN) → stronger, but still weak (CN^-)

Base → **Conjugate Acid**
 strong (OH^-) → very weak (H_2O)
 weak (NH_3) → stronger, but still weak (NH_4^+)

In Brønsted-Lowry terminology, anions of strong acids are extremely weak bases, whereas anions of weak acids are stronger bases (see Section 10-4). To refresh your memory, consider the following examples.

Nitric acid, a common strong acid, is essentially completely ionized in dilute aqueous solution. Dilute aqueous solutions of HNO_3 contain equal concentrations of H_3O^+ and NO_3^- ions. In dilute aqueous solution, nitrate ions show almost no tendency to react with H_3O^+ ions to form nonionized HNO_3 ; thus, NO_3^- is a very weak base.



On the other hand, acetic acid (a weak acid) is only slightly ionized in dilute aqueous solution. Acetate ions have a strong tendency to react with H_3O^+ to form CH_3COOH molecules.



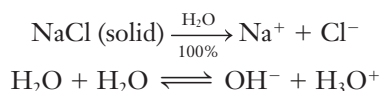
Hence, the CH_3COO^- ion is a stronger base than the NO_3^- ion, but it is still weak.

In dilute solutions, strong acids and strong bases are completely ionized or dissociated. In the following sections, we consider dilute aqueous solutions of salts. Based on our classification of acids and bases, we can identify four different kinds of salts.

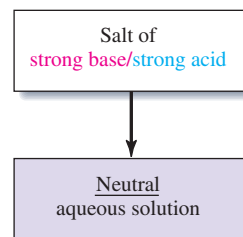
1. Salts of strong bases and strong acids
2. Salts of strong bases and weak acids
3. Salts of weak bases and strong acids
4. Salts of weak bases and weak acids

18-7 Salts of Strong Bases and Strong Acids

We could also describe these as salts that contain the cation of a strong base and the anion of a strong acid. Salts derived from strong bases and strong acids give *neutral* solutions because neither the cation nor the anion reacts appreciably with H_2O . Consider an aqueous solution of NaCl , which is the salt of the strong base NaOH and the strong acid HCl . Sodium chloride is ionic in the solid state and dissociates into hydrated ions ($\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$) in H_2O . H_2O ionizes slightly to produce equal concentrations of H_3O^+ and OH^- ions.



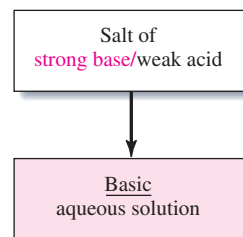
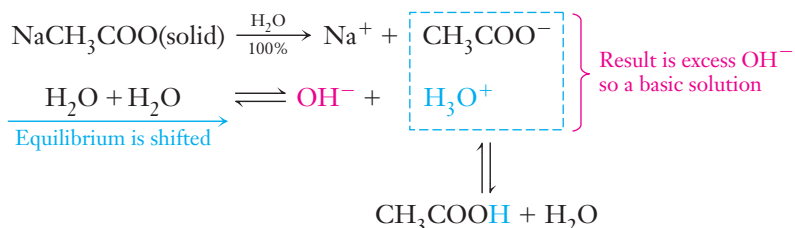
We see that aqueous solutions of NaCl contain four ions, Na^+ , Cl^- , H_3O^+ and OH^- . The cation of the salt, Na^+ , is such a weak acid that it does not react appreciably with water. The anion of the salt, Cl^- , is such a weak base that it does not react appreciably with water. Solutions of salts of strong bases and strong acids are therefore *neutral* because neither ion of such a salt reacts to upset the $\text{H}_3\text{O}^+/\text{OH}^-$ balance in water.



The salt of a strong acid and a strong base is often referred to as a *neutral salt*.

18-8 Salts of Strong Bases and Weak Acids

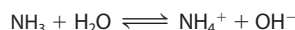
When salts derived from strong bases and weak acids are dissolved in water, the resulting solutions are always basic. This is because anions of weak acids react with water to form hydroxide ions. Consider a solution of sodium acetate, NaCH_3COO , which is the salt of the strong base NaOH and the weak acid CH_3COOH (acetic acid). It is soluble and dissociates completely in water.



Though the salt of a strong base and a weak acid is not strictly included in the definition of a basic salt (see Section 10-9), many chemists refer to such a salt as a *weakly basic salt*.

Acetate ion is the conjugate base of a *weak* acid, CH_3COOH . Thus, it reacts to some extent with H_3O^+ to form CH_3COOH . As H_3O^+ is removed from the solution, causing more H_2O to ionize, an excess of OH^- builds up. So the solution becomes basic. The net

► This is like the reaction of a molecular weak base



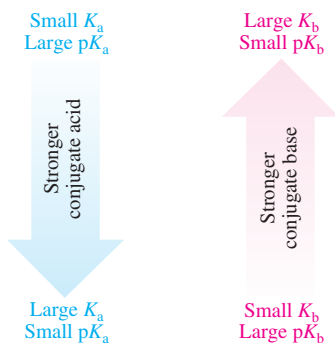
(excess OH^- is produced; the solution becomes basic)

STOP & THINK

Just as we can write a K_b expression to describe the extent of ionization of NH_3 , we can do the same for the acetate ion. The reaction of NH_3 with H_2O is called an *ionization* because a neutral base reacts with water to produce the NH_4^+ and OH^- ions. It is also a *hydrolysis* reaction.

► Base hydrolysis constants, K_b values, for anions of weak acids can be determined experimentally. The values obtained from experiments agree with the calculated values. Please note that this K_b refers to a reaction in which the anion of a weak acid acts as a base.

► For conjugate acid–base pairs:



result of the preceding equations can be written as a single equation. This equation describes the *hydrolysis of acetate ions*.



The equilibrium constant for this reaction is called a (base) *hydrolysis constant*, or K_b for CH_3COO^- .

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad (K_b \text{ for } \text{CH}_3\text{COO}^-)$$

We can evaluate this equilibrium constant from other known expressions. Multiply the preceding expression by $[\text{H}_3\text{O}^+]/[\text{H}_3\text{O}^+]$ to give

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{[\text{CH}_3\text{COOH}]}{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]} \times \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{1}$$

We see that

$$K_b = \frac{1}{K_a(\text{CH}_3\text{COOH})} \times \frac{K_w}{1} = \frac{K_w}{K_a(\text{CH}_3\text{COOH})} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

which gives

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = 5.6 \times 10^{-10}$$

We have calculated K_b , the hydrolysis constant for the acetate ion, CH_3COO^- , using the K_a value for the acid from which the anion was formed.

We can do the same kind of calculations for the anion of any weak monoprotic acid and find that $K_b = K_w/K_a$, where K_a refers to the ionization constant for the weak monoprotic acid from which the anion is derived.

This equation can be rearranged to

$$K_w = K_a K_b \quad (\text{valid for any conjugate acid–base pair in aqueous solution})$$

If either K_a or K_b is known, the other can be calculated.

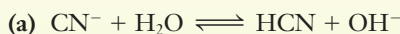
EXAMPLE 18-19 K_b for the Anion of a Weak Acid

(a) Write the equation for the reaction of the base CN^- with water. (b) The value of the ionization constant for hydrocyanic acid, HCN , is 4.0×10^{-10} . What is the value of K_b for the cyanide ion, CN^- ?

Plan

- (a) The base CN^- accepts H^+ from H_2O to form the weak acid HCN and OH^- ions.
 (b) We know that $K_a K_b = K_w$. So we solve for K_b and substitute into the equation.

Solution



(b) We are given $K_a = 4.0 \times 10^{-10}$ for HCN , and we know that $K_w = 1.0 \times 10^{-14}$.

$$K_{b(\text{CN}^-)} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5}$$

You should now work Exercises 74 and 76.

EXAMPLE 18-20 Calculations Based on Hydrolysis

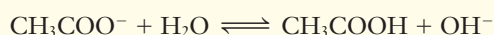
Calculate $[\text{OH}^-]$, pH, and the percent hydrolysis for 0.10 *M* solutions of (a) sodium acetate, NaCH_3COO , and (b) sodium cyanide, NaCN .

Plan

We recall that all sodium salts are soluble and that all soluble ionic salts are completely dissociated in H_2O . We recognize that both NaCH_3COO and NaCN are salts of strong bases (which provide the cation) and weak acids (which provide the anion). The anions in such salts hydrolyze to give basic solutions. In the preceding text we determined that K_b for $\text{CH}_3\text{COO}^- = 5.6 \times 10^{-10}$, and in Example 18-19 we determined that K_b for $\text{CN}^- = 2.5 \times 10^{-5}$. As we have done before, we first write the appropriate chemical equation and equilibrium constant expression. Then we complete the reaction summary, substitute the algebraic representations of equilibrium concentrations into the equilibrium constant expression, and solve for the desired concentration(s).

Solution

- (a) The overall equation for the reaction of CH_3COO^- with H_2O and its equilibrium constant expression are



$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = 5.6 \times 10^{-10}$$

Let $x = \text{mol/L}$ of CH_3COO^- that hydrolyzes. Then $x = [\text{CH}_3\text{COOH}] = [\text{OH}^-]$.

	CH_3COO^-	+	H_2O	$\rightleftharpoons$	CH_3COOH	+	OH^-
initial	0.10 <i>M</i>				0 <i>M</i>		$\approx 0 \text{ M}$
change due to rxn	$-x \text{ M}$				$+x \text{ M}$		$+x \text{ M}$
at equil	$(0.10 - x) \text{ M}$				$x \text{ M}$		$x \text{ M}$

Because the value of K_b (5.6×10^{-10}) is quite small, we know that the reaction does not go very far. We can assume $x \ll 0.10$, so $(0.10 - x) \approx 0.10$; this lets us simplify the equation to

$$5.6 \times 10^{-10} = \frac{(x)(x)}{0.10} \quad \text{so} \quad x = 7.5 \times 10^{-6}$$

$$x = 7.5 \times 10^{-6} \text{ M} = [\text{OH}^-]; \text{ so } \text{pOH} = 5.12 \quad \text{and} \quad \text{pH} = 8.88$$

$$\text{pH} = 14 - \text{pOH}$$

The 0.10 *M* NaCH_3COO solution is distinctly basic.

$$\begin{aligned} \% \text{ hydrolysis} &= \frac{[\text{CH}_3\text{COO}^-]_{\text{hydrolyzed}}}{[\text{CH}_3\text{COO}^-]_{\text{initial}}} \times 100\% = \frac{7.5 \times 10^{-6} \text{ M}}{0.10 \text{ M}} \times 100\% \\ &= 0.0075\% \text{ hydrolysis} \end{aligned}$$

- (b) Perform the same kind of calculation for 0.10 *M* NaCN . Let $y = \text{mol/L}$ of CN^- that hydrolyzes. Then $y = [\text{HCN}] = [\text{OH}^-]$.

	CN^-	+	H_2O	$\rightleftharpoons$	HCN	+	OH^-
initial	0.10 <i>M</i>				0 <i>M</i>		$\approx 0 \text{ M}$
change due to rxn	$-y \text{ M}$				$+y \text{ M}$		$+y \text{ M}$
at equil	$(0.10 - y) \text{ M}$				$y \text{ M}$		$y \text{ M}$

$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = 2.5 \times 10^{-5}$$

STOP & THINK

If we did not know either K_b value, we could use $K_{a(\text{CH}_3\text{COOH})}$ to find $K_{b(\text{CH}_3\text{COO}^-)}$, or $K_{a(\text{HCN})}$ to find $K_{b(\text{CN}^-)}$.



A The pH of 0.10 M NaCH₃COO is 8.88.



Beckman Instruments

B The pH of 0.10 M NaCN is 11.20.

An inert solid has been suspended in the liquids to improve the quality of these photographs.

Substituting into this expression and realizing that $(0.10 - y) \approx 0.10$ gives

$$\frac{(y)(y)}{(0.10)} = 2.5 \times 10^{-5} \quad \text{so} \quad y = 1.6 \times 10^{-3} M$$

$$y = [\text{OH}^-] = 1.6 \times 10^{-3} M \quad \text{pOH} = 2.80 \quad \text{and} \quad \text{pH} = 11.20$$

The 0.10 M NaCN solution is even more basic (about 210 times) than the 0.10 M NaCH₃COO solution in Part (a).

$$\begin{aligned} \% \text{ hydrolysis} &= \frac{[\text{CN}^-]_{\text{hydrolyzed}}}{[\text{CN}^-]_{\text{initial}}} \times 100\% = \frac{1.6 \times 10^{-3} M}{0.10 M} \times 100\% \\ &= 1.6\% \text{ hydrolysis} \end{aligned}$$

You should now work Exercises 79 and 80.

The 0.10 M solution of NaCN is considerably more basic than the 0.10 M solution of NaCH₃COO because CN[−] is a much stronger base than CH₃COO[−]. This is expected because HCN is a much weaker acid than CH₃COOH; the K_b for CN[−] is much larger than the K_b for CH₃COO[−].

The percent hydrolysis for 0.10 M CN[−] (1.6%) is about 210 times greater than the percent hydrolysis for 0.10 M CH₃COO[−] (0.0075%). In Table 18-9 we compare 0.10 M solutions of CH₃COO[−], CN[−], and NH₃ (the familiar molecular weak base). We see that CH₃COO[−] is a much weaker base than NH₃, whereas CN[−] is a slightly stronger base than NH₃.

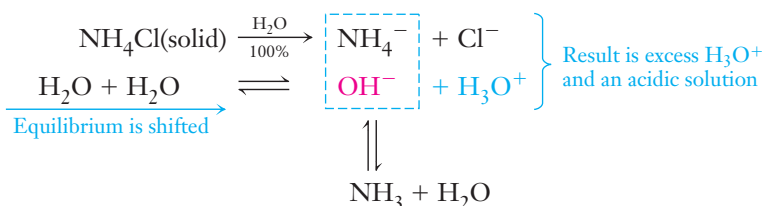
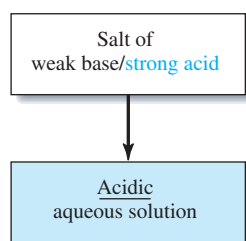
Table 18-9 Data for 0.10 M Solutions of NaCH₃COO, NaCN, and NH₃

	0.10 M NaCH ₃ COO	0.10 M NaCN	0.10 M aq NH ₃
K_a for parent acid	1.8×10^{-5}	4.0×10^{-10}	
K_b for anion	5.6×10^{-10}	2.5×10^{-5}	K_b for NH ₃ = 1.8×10^{-5}
[OH [−]]	$7.5 \times 10^{-6} M$	$1.6 \times 10^{-3} M$	$1.3 \times 10^{-3} M$
% hydrolysis	0.0075%	1.6%	1.3% ionized
pH	8.88	11.20	11.11

18-9 Salts of Weak Bases and Strong Acids

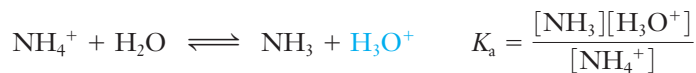
The second common kind of hydrolysis reaction involves the reaction of the cation of a weak base with water to form nonionized molecules of the weak base and H₃O⁺ ions. This upsets the H₃O⁺/OH[−] balance in water, giving an excess of H₃O⁺ and making such solutions *acidic*. Consider a solution of ammonium chloride, NH₄Cl, the salt of aqueous NH₃ and HCl.

► Ammonium chloride is an ionic salt that is soluble in water.



Unless otherwise noted, all content on this page is © Cengage Learning.

Ammonium ions from NH_4Cl react to some extent with OH^- to form nonionized NH_3 and H_2O molecules. This reaction removes OH^- from the system, so it causes more H_2O to ionize to produce an excess of H_3O^+ and an acidic solution. The net result of the preceding equations can be written as a single equation with its equilibrium constant expression.



The expression $K_w = K_a K_b$ is valid for *any* conjugate acid-base pair in aqueous solution. We use it for the $\text{NH}_4^+/\text{NH}_3$ pair.

$$K_{a(\text{NH}_4^+)} = \frac{K_w}{K_{b(\text{NH}_3)}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

The fact that K_a for the ammonium ion, NH_4^+ , is the same as K_b for the acetate ion should not be surprising. Recall that the ionization constants for CH_3COOH and aqueous NH_3 are equal (by coincidence). Thus, we expect CH_3COO^- to hydrolyze to the same extent as NH_4^+ does.

► Many chemists refer to the salt produced by the reaction of a weak base and a strong acid as a *weakly acidic salt*.

► Similar equations can be written for cations derived from other weak bases such as CH_3NH_3^+ and $(\text{CH}_3)_2\text{NH}_2^+$.

► If you wish to derive $K_a = K_w/K_b$ for this case, multiply the K_b expression by $[\text{OH}^-]/[\text{OH}^-]$ and simplify. This is similar to the derivation that was shown in detail for K_b in Section 18-8.

EXAMPLE 18-21 pH of a Soluble Salt of a Strong Acid and a Weak Base

Calculate the pH of a 0.20 M solution of ammonium nitrate, NH_4NO_3 .

Plan

We recognize that NH_4NO_3 is the salt of a weak base, NH_3 , and a strong acid, HNO_3 , and that the cations of such salts hydrolyze to give acidic solutions. From our earlier calculations, we know that K_a for $\text{NH}_4^+ = 5.6 \times 10^{-10}$. We proceed as we did in Example 18-20.

Solution

The cation of the weak base reacts with H_2O . Let $x = \text{mol/L}$ of NH_4^+ that hydrolyzes. Then $x = [\text{NH}_3] = [\text{H}_3\text{O}^+]$.

	NH_4^+	+	H_2O	$\rightleftharpoons$	NH_3	+	H_3O^+	
initial	0.20 M				0 M		≈ 0 M	
change due to rxn	$-x$ M				$+x$ M		$+x$ M	
at equil	$(0.20 - x)$ M				x M		x M	

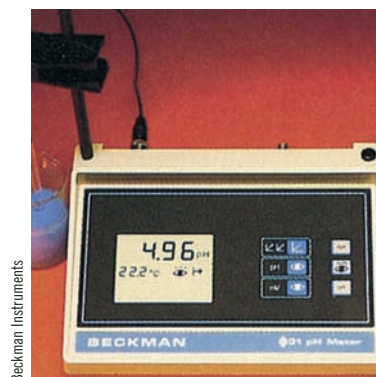
Substituting into the K_a expression gives

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{(x)(x)}{0.20 - x} = 5.6 \times 10^{-10}$$

Making the usual simplifying assumption gives $x = 1.1 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$ and **pH = 4.96**. The 0.20 M NH_4NO_3 solution is distinctly acidic.

You should now work Exercise 86.

► Ammonium nitrate is widely used as a fertilizer because of its high nitrogen content. It contributes to soil acidity.



The pH of 0.20 M NH_4NO_3 solution is 4.96.

18-10 Salts of Weak Bases and Weak Acids

Salts of weak bases and weak acids are the fourth class of salts. Most are soluble. Salts of weak bases and weak acids contain cations that would give acidic solutions and also contain anions that would give basic solutions. Will solutions of such salts be neutral, basic, or acidic? They may be any one of the three depending on the relative strengths of the weak molecular acid and weak molecular base from which each salt is derived. Thus, salts of this class may be divided into three types that depend on the relative strengths of their parent weak bases and weak acids.

CHEMISTRY IN USE

Taming Dangerous Acids with Harmless Salts

From yellowing paper in old books and newsprint to heartburn and environmental spills, many Americans encounter the effects of unwanted or excessive amounts of acid. Neutralizing unwanted acids with hydroxide bases might appear to be a good way to combat these acids. But even more effective chemicals exist that can neutralize acids without the risks posed by hydroxide bases. These acid-neutralizing chemicals are salts of weak acids and strong bases. Such salts can neutralize acids because hydrolysis makes their aqueous solutions basic. More importantly, there is a significant advantage in using relatively harmless salts such as sodium hydrogen carbonate (baking soda) rather than stronger bases such as sodium hydroxide (lye). For example, if we used too much sodium hydroxide to neutralize sulfuric acid spilled from a car battery, any excess lye left behind would pose an environmental and human health threat about equal to that of the spilled sulfuric acid. (Lye is the major ingredient in such commercial products as oven cleaners and Drano.) We would not be concerned, however, if a little baking soda were left on the ground after the sulfuric acid from the car battery had been neutralized.

The same principle applies to acid indigestion. Rather than swallow lye (ugh!) or some other strong base to neutralize excess stomach acid, most people take antacids. Antacids typically contain salts such as calcium carbonate, sodium hydrogen carbonate (sodium bicarbonate), and magnesium carbonate, all of which are salts of weak acids. These salts hydrolyze to

form hydroxide ions that reduce the degree of acidity in the stomach. Physicians also prescribe these and similar salts to treat peptic ulcers. The repeated use of antacids should always be under the supervision of a physician.

Salts of weak acids and strong bases can be used effectively against a major acid spill in much the same way they are used against sulfuric acid from a car battery or excess stomach acid. In a recent major acid spill, a tank car filled with nitric acid was punctured by the coupling of another rail car, spilling 22,000 gallons of concentrated nitric acid onto the ground. Several thousand residents living near the spill were evacuated. There were no fatalities or serious injuries, and there was no major environmental damage; resident firefighters neutralized the concentrated nitric acid by using airport snow blowers to spread *relatively* harmless sodium carbonate (washing soda) over the contaminated area.

Salts of weak acids and strong bases are also being used to combat the destructive aging process of paper. Think how serious this problem is for the Library of Congress, which loses 70,000 books each year to the acid-promoted decomposition of aging paper. Many of the twenty million books in the Library of Congress have a life expectancy of only 25 to 40 years. Paper ages because of the hydrolysis of aluminum sulfate. Aluminum sulfate has been used in the paper manufacturing process since the 1850s because it is an inexpensive sizing compound (it keeps ink from spreading out on paper). Aluminum sulfate is the salt of an insoluble weak base and a strong acid; it hydrolyzes in the water in paper (typically 4–7% H_2O) to give an acidic environment. The acid slowly eats away at cellulose fibers, which causes the paper to turn yellow and eventually disintegrate. To combat this aging, the Library of Congress individually treats its collections with solutions of salts of weak acids and strong bases at great cost. Meanwhile, the paper industry is fighting this aging process by increasing its output of alkaline paper. Some alkaline paper contains calcium carbonate, the same salt found in several brands of antacids. Calcium carbonate increases the pH of paper to between 7.5 and 8.5. Special manufacturing techniques produce calcium carbonate that is very fine and that has uniform particle size. Alkaline papers are expected to last about 300 years, in contrast to the average 25- to 40-year life expectancy of standard acidic paper.

Salts that hydrolyze to produce basic solutions can settle upset stomachs, prevent yellowing pages, and neutralize major and minor acid spills. A knowledge of hydrolysis is very useful and has many applications.

RONALD DELORENZO

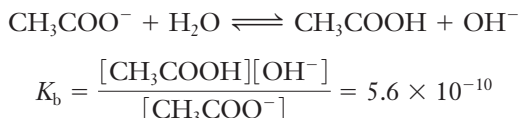


Salts of Weak Bases and Weak Acids for Which Parent $K_b = \text{Parent } K_a$

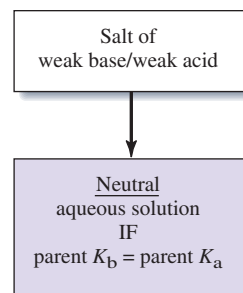
The most common salt of this type is ammonium acetate, $\text{NH}_4\text{CH}_3\text{COO}$, the salt of aqueous NH_3 and CH_3COOH . The ionization constants for both aqueous NH_3 and CH_3COOH are 1.8×10^{-5} . We know that ammonium ions react with water to produce H_3O^+ .



We also recall that acetate ions react with water to produce OH^- .



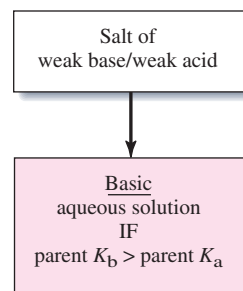
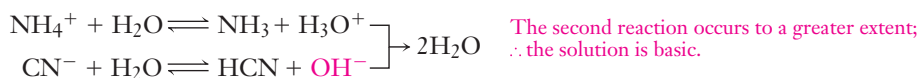
Because these K values are equal, the NH_4^+ produces just as many H_3O^+ ions as the CH_3COO^- produces OH^- ions. Thus, we predict that ammonium acetate solutions are neutral, and they are. There are very few salts, however, that have cations and anions with equal K values.



Salts of Weak Bases and Weak Acids for Which Parent $K_b > \text{Parent } K_a$

Salts of weak bases and weak acids for which K_b is greater than K_a are always basic because the anion of the weaker acid hydrolyzes to a greater extent than the cation of the stronger base.

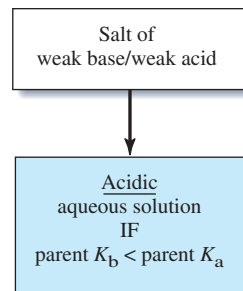
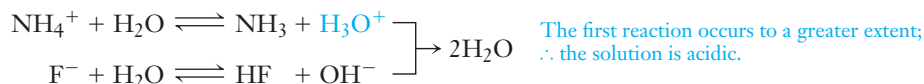
Consider NH_4CN , ammonium cyanide. K_a for HCN (4.0×10^{-10}) is much smaller than K_b for NH_3 (1.8×10^{-5}), so K_b for CN^- (2.5×10^{-5}) is much larger than K_a for NH_4^+ (5.6×10^{-10}). This tells us that the CN^- ions hydrolyze to a much greater extent than do NH_4^+ ions, and so ammonium cyanide solutions are distinctly basic. Stated differently, CN^- is much stronger as a base than NH_4^+ is as an acid.



Salts of Weak Bases and Weak Acids for Which Parent $K_b < \text{Parent } K_a$

Salts of weak bases and weak acids for which K_b is less than K_a are acidic because the cation of the weaker base hydrolyzes to a greater extent than the anion of the stronger acid. Consider ammonium fluoride, NH_4F , the salt of aqueous ammonia and hydrofluoric acid.

K_b for aqueous NH_3 is 1.8×10^{-5} and K_a for HF is 7.2×10^{-4} . So the K_a value for NH_4^+ (5.6×10^{-10}) is slightly larger than the K_b value for F^- (1.4×10^{-11}). This tells us that NH_4^+ ions hydrolyze to a slightly greater extent than F^- ions. In other words, NH_4^+ is slightly stronger as an acid than F^- is as a base. Ammonium fluoride solutions are slightly acidic.



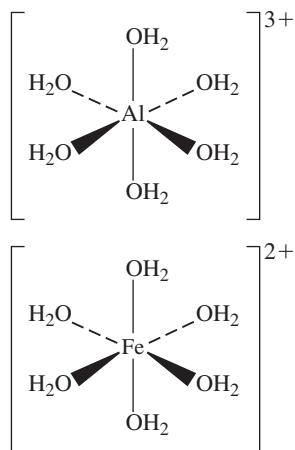
EXAMPLE 18-22 Predicting Which Salts Are Acidic and Which Are Basic

Classify each of the following soil additives as an acidic salt, a neutral salt, or a basic salt:

(a) $(\text{NH}_4)_2\text{SO}_4$; (b) NH_4NO_3 ; (c) Na_2CO_3 .

Plan

We recognize these salts as being the products of acid/base reactions. We can categorize each parent acid and base as being stronger or weaker. We then predict the properties of each salt based upon the strength of its parent acid and parent base.



A Lewis structures of hydrated aluminum ions, $[\text{Al}(\text{OH}_2)_6]^{3+}$, and hydrated iron(II) ions, $[\text{Fe}(\text{OH}_2)_6]^{2+}$



B Ball-and-stick model of either of these ions

Figure 18-3 Some hydrated ions.

Solution

- (a) $(\text{NH}_4)_2\text{SO}_4$ is the salt formed by the reaction of NH_3 (a weak base) and H_2SO_4 (a strong acid). Because H_2SO_4 is stronger as an acid than NH_3 is as a base, $(\text{NH}_4)_2\text{SO}_4$ is an acidic salt.
- (b) NH_4NO_3 is the salt formed by the reaction of NH_3 (a weak base) and HNO_3 (a strong acid). Because HNO_3 is stronger as an acid than NH_3 is as a base, NH_4NO_3 is an acidic salt.
- (c) Na_2CO_3 is the salt formed by the reaction of NaOH (a strong base) and H_2CO_3 (a weak acid). Because NaOH is stronger as a base than H_2CO_3 is as an acid, Na_2CO_3 is a basic salt.

You should now work Exercise 102.

18-11 Salts That Contain Small, Highly Charged Cations

Solutions of certain common salts of strong acids are acidic. For this reason, many homeowners apply iron(II) sulfate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, or aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, to the soil around “acid-loving” plants such as azaleas, camellias, and hollies. You have probably tasted the sour, “acid” taste of alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, a substance that is frequently added to pickles.

Each of these salts contains a small, highly charged cation and the anion of a strong acid. Solutions of such salts are acidic because these cations hydrolyze to produce excess hydronium ions. Consider aluminum chloride, AlCl_3 , as a typical example. When solid anhydrous AlCl_3 is added to water, the water becomes very warm as the Al^{3+} ions become hydrated in solution. In many cases, the interaction between positively charged ions and the negative ends of polar water molecules is so strong that salts crystallized from aqueous solution contain definite numbers of water molecules. Salts containing Al^{3+} , Fe^{2+} , Fe^{3+} , and Cr^{3+} ions usually crystallize from aqueous solutions with six water molecules bonded (coordinated) to each metal ion. These salts contain the hydrated cations $[\text{Al}(\text{OH}_2)_6]^{3+}$, $[\text{Fe}(\text{OH}_2)_6]^{2+}$, $[\text{Fe}(\text{OH}_2)_6]^{3+}$, and $[\text{Cr}(\text{OH}_2)_6]^{3+}$, respectively, in the solid state. Such species also exist in aqueous solutions. Each of these species is octahedral, meaning that the metal ion (M^{n+}) is located at the center of a regular octahedron, and the O atoms in six H_2O molecules are located at the corners (Figure 18-3). In the metal–oxygen bonds of the hydrated cation, electron density is decreased around the O end of each H_2O molecule by the positively charged metal ion. This weakens the $\text{H}-\text{O}$ bonds in coordinated H_2O molecules relative to the $\text{H}-\text{O}$ bonds in noncoordinated H_2O molecules. Consequently, the coordinated H_2O molecules can donate H^+ to solvent H_2O molecules to form H_3O^+ ions. This produces acidic solutions (Figure 18-4).

The equation for the hydrolysis of hydrated Al^{3+} is written as follows.

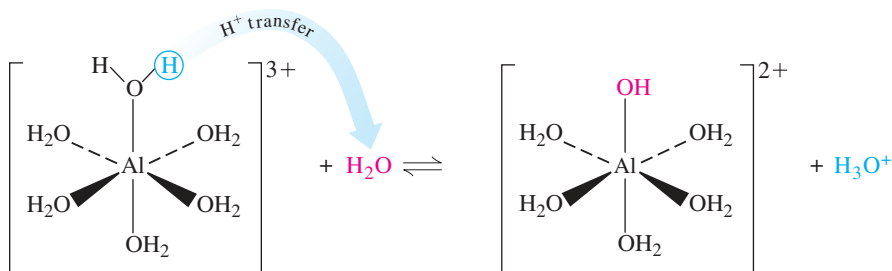
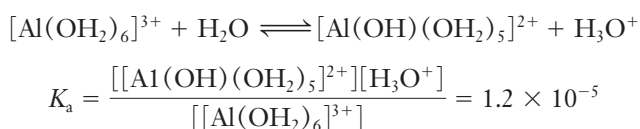


Figure 18-4 Hydrolysis of hydrated aluminum ions produces H_3O^+ by the transfer of a proton from a coordinated H_2O molecule to a noncoordinated one.

Removing one H^+ converts a coordinated water molecule to a coordinated hydroxide ion and decreases the positive charge on the hydrated species.

Hydrolysis of hydrated small, highly charged cations may occur beyond the first step. In many cases these reactions are quite complex. They may involve two or more cations reacting with each other to form large polymeric species. For most common hydrated cations, consideration of the first hydrolysis constant is adequate for our calculations.

EXAMPLE 18-23 Percent Hydrolysis

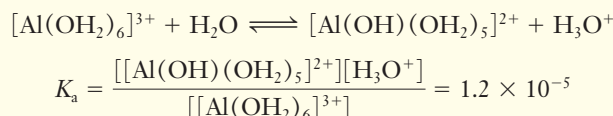
Calculate the pH and percent hydrolysis in 0.10 M AlCl_3 solution. $K_a = 1.2 \times 10^{-5}$ for $[\text{Al}(\text{OH}_2)_6]^{3+}$ (often abbreviated Al^{3+}).

Plan

We recognize that AlCl_3 produces a hydrated, small, highly charged cation that hydrolyzes to give an acidic solution. We represent the equilibrium concentrations and proceed as we did in earlier examples.

Solution

The equation for the reaction and its hydrolysis constant can be represented as



Let $x = \text{mol/L}$ of $[\text{Al}(\text{OH}_2)_6]^{3+}$ that hydrolyzes. Then $x = [\text{Al}(\text{OH})(\text{OH}_2)_5]^{2+} = [\text{H}_3\text{O}^+]$.

	$[\text{Al}(\text{OH}_2)_6]^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{Al}(\text{OH})(\text{OH}_2)_5]^{2+} + \text{H}_3\text{O}^+$		
initial	0.10 M		
change due to rxn	$-x \text{ M}$	$+x \text{ M}$	$+x \text{ M}$
at equil	$(0.10 - x) \text{ M}$	$x \text{ M}$	$x \text{ M}$

$$\frac{(x)(x)}{(0.10 - x)} = 1.2 \times 10^{-5} \text{ so } x = 1.1 \times 10^{-3}$$

$[\text{H}_3\text{O}^+] = 1.1 \times 10^{-3} \text{ M}$, pH = 2.96; the solution is quite acidic.

$$\% \text{ hydrolysis} = \frac{[\text{Al}^{3+}]_{\text{hydrolyzed}}}{[\text{Al}^{3+}]_{\text{initial}}} \times 100\% = \frac{1.1 \times 10^{-3} \text{ M}}{0.10 \text{ M}} \times 100\% = 1.1\% \text{ hydrolyzed}$$

As a reference point, CH_3COOH is 1.3% ionized in 0.10 M solution (Example 18-11). In 0.10 M solution, AlCl_3 is 1.1% hydrolyzed. The acidities of the two solutions are very similar.

You should now work Exercise 92.



Charles D. Winters

The blue color and the acidity of a 0.10 M CuSO_4 solution are both due to the hydrated Cu^{2+} ion.

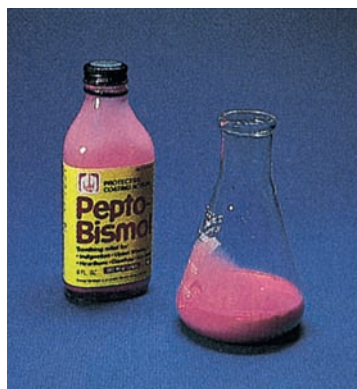
► Recall that x represents the concentration of Al^{3+} that hydrolyzes.

► The pH of 0.10 M AlCl_3 is 2.96. The pH of 0.10 M CH_3COOH is 2.89.

Smaller, more highly charged cations are stronger acids than larger, less highly charged cations (Table 18-10). This is because the smaller, more highly charged cations interact with coordinated water molecules more strongly.

For isoelectronic cations in the same period in the periodic table, the smaller, more highly charged cation is the stronger acid. (Compare K_a values for hydrated Li^+ and Be^{2+} and for hydrated Na^+ , Mg^{2+} , and Al^{3+} .) For cations with the same charge from the same group in the periodic table, the smaller cation hydrolyzes to a greater extent. (Compare K_a values for hydrated Be^{2+} and Mg^{2+} .) If we compare cations of the same element in different oxidation states, the smaller, more highly charged cation is the stronger acid. (Compare K_a values for hydrated Fe^{2+} and Fe^{3+} and for hydrated Co^{2+} and Co^{3+} .)

Unless otherwise noted, all content on this page is © Cengage Learning.



Pepto-Bismol contains $\text{BiO}(\text{HOC}_4\text{H}_6\text{COO})$, bismuth subsalicylate, a *hydrolyzed* bismuth salt. Such salts “coat” polar surfaces such as glass and the lining of the stomach.

Table 18-10 Ionic Radii and Hydrolysis Constants for Some Cations

Cation	Ionic Radius (Å)	Hydrated Cation	K_a
Li^+	0.90	$[\text{Li}(\text{OH}_2)_4]^+$	1×10^{-14}
Be^{2+}	0.59	$[\text{Be}(\text{OH}_2)_4]^{2+}$	1.0×10^{-5}
Na^+	1.16	$[\text{Na}(\text{OH}_2)_6]^+$	10^{-14}
Mg^{2+}	0.85	$[\text{Mg}(\text{OH}_2)_6]^{2+}$	3.0×10^{-12}
Al^{3+}	0.68	$[\text{Al}(\text{OH}_2)_6]^{3+}$	1.2×10^{-5}
Fe^{2+}	0.76	$[\text{Fe}(\text{OH}_2)_6]^{2+}$	3.0×10^{-10}
Fe^{3+}	0.64	$[\text{Fe}(\text{OH}_2)_6]^{3+}$	4.0×10^{-3}
Co^{2+}	0.74	$[\text{Co}(\text{OH}_2)_6]^{2+}$	5.0×10^{-10}
Co^{3+}	0.63	$[\text{Co}(\text{OH}_2)_6]^{3+}$	1.7×10^{-2}
Cu^{2+}	0.96	$[\text{Cu}(\text{OH}_2)_6]^{2+}$	1.0×10^{-8}
Zn^{2+}	0.74	$[\text{Zn}(\text{OH}_2)_6]^{2+}$	2.5×10^{-10}
Hg^{2+}	1.10	$[\text{Hg}(\text{OH}_2)_6]^{2+}$	8.3×10^{-7}
Bi^{3+}	0.74	$[\text{Bi}(\text{OH}_2)_6]^{3+}$	1.0×10^{-2}

KEY TERMS

Amines Derivatives of ammonia in which one or more hydrogen atoms has been replaced by organic groups.

Electrolytes Compounds that ionize (or dissociate into their constituent ions) when dissolved in water to produce aqueous solutions that conduct an electric current.

Hydrolysis The reaction of a substance with water.

Hydrolysis constant An equilibrium constant for a hydrolysis reaction.

Indicator An organic compound that exhibits different colors in solutions of different acidities.

Ion product for water An equilibrium constant for the ionization of water,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

Ionization constant An equilibrium constant for the ionization of a weak electrolyte.

Monoprotic acid An acid that can form only one hydronium ion per molecule; may be strong or weak.

Nonelectrolytes Compounds that do not ionize (or dissociate into their constituent ions) when dissolved in water to

produce aqueous solutions that will not conduct an electric current.

pH The negative logarithm of the concentration (mol/L) of the H_3O^+ (or H^+) ion; the commonly used scale ranges from 0 to 14.

$\text{p}K_a$ The negative logarithm of K_a , the ionization constant for a weak acid.

$\text{p}K_b$ The negative logarithm of K_b , the ionization constant for a weak base.

$\text{p}K_w$ The negative logarithm of the ion product for water.

pOH The negative logarithm of the concentration (mol/L) of the OH^- ion; the commonly used scale ranges from 14 to 0.

Polyprotic acid An acid that can form two or more hydronium ions per molecule.

Solvolysis The reaction of a substance with the solvent in which it is dissolved.

Strong electrolytes Compounds that ionize (or dissociate into their constituent ions) completely, or nearly completely, when dissolved in water to produce aqueous solutions that conduct an electric current.

EXERCISES

Molecular Reasoning exercises

More Challenging exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Review of Strong Electrolytes

- List names and formulas for (a) seven strong acids; (b) six weak bases; (c) the common strong bases; (d) ten soluble ionic salts.
- (a) How are a strong acid and a weak acid similar? How are they different? (b) How are a strong base and a weak base similar? How are they different?

- Which of the following are strong electrolytes: a Group 1A hydroxide, a Group 3A hydroxide, $\text{Cu}(\text{OH})_2$, $\text{Be}(\text{OH})_2$, H_3AsO_3 , HI , HF , H_2SO_3 , H_3PO_4 , salts of a Group 1A metal?
- Calculate the molarity of each of the following solutions. (a) 25.65 g of NaCl in 250. mL of solution; (b) 75.5 g of H_2SO_4 in 1.00 L of solution; (c) 0.126 g of phenol, $\text{C}_6\text{H}_5\text{OH}$, in 1.00 L of solution.

Molecular Reasoning exercises

More Challenging exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

- Square brackets, [], are often used in mathematical statements in chemistry. What is the meaning associated with square brackets?
- Calculate the concentrations of the constituent ions in solutions of the following compounds in the indicated concentrations: (a) 0.45 *M* HBr; (b) 0.045 *M* KOH; (c) 0.0112 *M* CaCl₂.
- Calculate the concentrations of the constituent ions in solutions of the following compounds in the indicated concentrations: (a) 0.0105 *M* Sr(OH)₂; (b) 0.0105 *M* HClO₃; (c) 0.0105 *M* K₂SO₄.
- Calculate the concentrations of the constituent ions in the following solutions: (a) 1.25 g of KOH in 1.50 L of solution; (b) 0.2505 g of Ba(OH)₂ in 250. mL of solution; (c) 1.26 g of Ca(NO₃)₂ in 100. mL of solution.
- Calculate the concentrations of the constituent ions in the following solutions: (a) 1.57 g of Al₂(SO₄)₃ in 425 mL of solution; (b) 45.8 g of CaCl₂·6H₂O in 5.00 L of solution; (c) 18.4 g of HBr in 675 mL of solution.
- (a) A sample of milk is found to have a pH of 6.50. What are the concentrations of H₃O⁺ and OH⁻ ions in this sample? (b) A sample of buttermilk has a pH of 4.50. Which sample is more acidic? (c) By what factor? (d) Activation of baking soda (as in the baking of biscuits) depends on an acidic environment. Which would be more effective in this process—milk or buttermilk? Why?



Charles D. Winters

The Autoionization of Water

- (a) Write a chemical equation showing the ionization of water. (b) Write the equilibrium constant expression for this equation. (c) What is the special symbol used for this equilibrium constant? (d) What is the relationship between [H⁺] and [OH⁻] in pure water? (e) How can this relationship be used to define the terms "acidic" and "basic"?
- Use *K_w* to explain the relationship between the hydronium ion concentration and the hydroxide ion concentration in aqueous solutions.
- (a) Why is the concentration of OH⁻ produced by the ionization of water neglected in calculating the concentration of OH⁻ in a 0.060 *M* solution of NaOH? (b) Demonstrate that the concentration of OH⁻ from H₂O can be neglected in the 0.060 *M* solution of NaOH.
- Calculate the concentrations of OH⁻ in the solutions described in Exercises 6(a), 7(b), and 9(c), and compare them with the OH⁻ concentration in pure water.
- Calculate the concentrations of H₃O⁺ in the solutions described in Exercises 6(b), 7(a), and 8(b), and compare them with the H₃O⁺ concentration in pure water.
- Calculate [OH⁻] that is in equilibrium with (a) [H₃O⁺] = 6.3 × 10⁻⁴ mol/L (b) [H₃O⁺] = 7.8 × 10⁻⁹ mol/L.
- Calculate the concentration of water in moles/liter. Using the ratio of the concentrations of hydronium ions in pure water (1 × 10⁻⁷ *M*) to water itself, calculate the number of hydronium ions for every 10 billion water molecules.
- The normal pH of human blood ranges from 7.35 to 7.45. Calculate the concentrations of H₃O⁺ and OH⁻ ions in human blood that has a pH of 7.45.
- Calculate the pH of (a) a 1.5 × 10⁻⁴ *M* solution of HClO₄, a strong acid, at 25°C and (b) 1.5 × 10⁻⁸ *M* solution of HCl at 25°C.
- Calculate the pH of the following solutions: (a) 2.0 × 10⁻¹ *M* HCl; (b) 0.050 *M* HNO₃; (c) 0.65 g·L⁻¹ HClO₄; (d) 9.8 × 10⁻⁴ *M* NaOH.
- Calculate the [H₃O⁺], [OH⁻], pH, and pOH in a 0.0548 *M* HCl solution.
- A solution of HNO₃ has a pH of 3.52. What is the molarity of the solution?
- Complete the following table. Is there an obvious relationship between pH and pOH? What is it?



Charles D. Winters

Solution	[H ₃ O ⁺]	[OH ⁻]	pH	pOH
0.25 <i>M</i> HI	_____	_____	_____	_____
0.067 <i>M</i> RbOH	_____	_____	_____	_____
0.020 <i>M</i> Ba(OH) ₂	_____	_____	_____	_____
0.00030 <i>M</i> HClO ₄	_____	_____	_____	_____

The pH and pOH Scales

- Write mathematical definitions for pH and pOH. What is the relationship between pH and pOH? How can pH be used to define the terms "acidic" and "basic"?
- Find the pH and pOH of solutions with the following [H⁺]. Classify each as acidic or basic. (a) 1.0 *M*; (b) 1.7 × 10⁻⁴ *M*; (c) 6.8 × 10⁻⁸ *M*; (d) 9.3 × 10⁻¹¹ *M*.



Molecular Reasoning exercises



More Challenging exercises

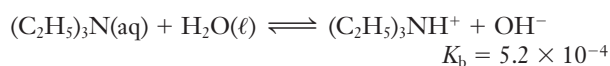
Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

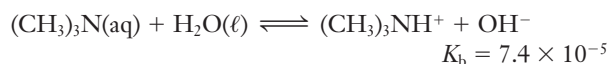
26. Calculate the following values for each solution.

Solution	[H ₃ O ⁺]	[OH ⁻]	pH	pOH
(a) 0.085 M NaOH	_____	_____	_____	_____
(b) 0.075 M HCl	_____	_____	_____	_____
(c) 0.075 M Ca(OH) ₂	_____	_____	_____	_____

27. What is the relationship between base strength and the value of K_b ? What is the relationship between acid strength and the value of pK_a ?
28. Predict which acid of each pair is the stronger acid. Briefly explain how you arrived at your answer. (a) H₃PO₄ or H₃AsO₄; (b) H₃AsO₃ or H₃AsO₄. (*Hint*: Review Chapter 10 and Appendix F.)
29. Predict which acid of each pair is the stronger acid. Briefly explain how you arrived at your answer. (a) H₂O or H₂S; (b) HOBr or HOCl. (*Hint*: Review Chapter 10 and Appendix F.)
30. Write a chemical equation that represents the ionization of a weak acid, HA. Write the equilibrium constant expression for this reaction. What is the special symbol used for this equilibrium constant?
31. What is the relationship between the strength of an acid and the numerical value of K_a ? What is the relationship between the acid strength and the value of pK_b ?
32. Because K_b is larger for triethylamine



than for trimethylamine



an aqueous solution of triethylamine should have a larger concentration of OH⁻ ion than an aqueous solution of trimethylamine of the same concentration. Confirm this statement by calculating the [OH⁻] for 0.018 M solutions of both weak bases.

33. The equilibrium constant of the following reaction is 1.35×10^{-15} .



D is deuterium, ²H. Calculate the pD of pure deuterium oxide (heavy water). What is the relationship between [D₃O⁺] and [OD⁻] in pure D₂O? Is pure D₂O acidic, basic, or neutral?

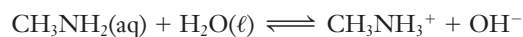
34. (a) What is the pH of pure water at body temperature, 37°C? Refer to Table 18-2. (b) Is this acidic, basic, or neutral? Why?
35. Fill in the blanks in this table for the given solutions.

Sol'n	Temp. (°C)	Concentration (mol/L)		pH
		[H ₃ O ⁺]	[OH ⁻]	
(a)	25	1.0×10^{-4}	_____	_____
(b)	0	_____	_____	2.75
(c)	60	_____	_____	7.00
(d)	25	_____	4.5×10^{-8}	_____

36. Write a chemical equation that represents the equilibrium between water and a weak base, B. Write the equilibrium constant expression for this reaction. What is the special symbol used for this equilibrium constant?
37. Complete the following table by appropriate calculations.

[H ₃ O ⁺]	pH	[OH ⁻]	pOH
(a) _____	4.84	_____	_____
(b) _____	10.61	_____	_____
(c) _____	_____	_____	2.90
(d) _____	_____	_____	9.47

38. A 0.0750 M solution of a monoprotic acid is known to be 1.07% ionized. What is the pH of the solution? Calculate the value of K_a for this acid.
39. A 0.075 M aqueous solution of a weak, monoprotic acid is 0.85% ionized. Calculate the value of the ionization constant, K_a , for this acid.
40. A 0.10 M solution of chloroacetic acid, ClCH₂CO₂H, has a pH of 1.95. Calculate K_a for the acid.
41. The pH of a 0.35 M solution of uric acid is 2.17. What is the value of K_a for uric acid, a monoprotic acid?
42. Calculate the concentrations of all the species present in a 0.52 M benzoic acid solution. (See Appendix F.)
43. Find the concentrations of the various species present in a 0.45 M solution of HOBr. What is the pH of the solution? (See Appendix F.)
44. Hydrofluoric acid can be used to etch glass. Calculate the pH of a 0.38 M HF solution.
45. To what volume should 1.00×10^2 mL of any weak acid, HA, with a concentration of 0.20 M be diluted to double the percentage ionization?
46. Calculate the pH and pOH of a household ammonia solution that contains 2.05 moles of NH₃ per liter of solution.
47. Calculate the percent ionization in a 0.56 M NH₃ solution.
48. What is the percent ionization in a 0.0751 M solution of formic acid, HCOOH?
49. What is the percent ionization in (a) a 0.150 M CH₃COOH solution, (b) a 0.0150 M CH₃COOH solution?
50. The K_a values for two weak acids are 7.2×10^{-5} and 4.2×10^{-10} , respectively. What are their pK_a values?
51. What is the concentration of OI⁻ in equilibrium with [H₃O⁺] = 0.045 mol/L and [HOI] = 0.527 mol/L?
52. Pyridine is 0.053% ionized in 0.00500 M solution. What is the pK_b of this monobasic compound?
53. A 0.068 M solution of benzamide has a pOH of 2.91. What is the value of pK_b for this monobasic compound?
54. In a 0.0100 M aqueous solution of methylamine, CH₃NH₂, the equilibrium concentrations of the species are [CH₃NH₂] = 0.0080 mol/L and [CH₃NH₃⁺] = [OH⁻] = 2.0×10^{-3} mol/L. Calculate K_b for this weak base.

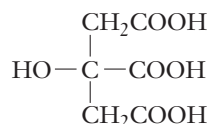


55. What is the concentration of NH₃ in equilibrium with [NH₄⁺] = 0.010 mol/L and [OH⁻] = 1.2×10^{-5} mol/L?
56. Calculate [OH⁻], percent ionization, and pH for (a) 0.25 M aqueous ammonia, (b) 0.25 M methylamine solution.

57. Calculate $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH, pOH, and percent ionization for 0.20 M aqueous ammonia.

Polyprotic Acids

58. Calculate the concentrations of the various species in a 0.100 M H_3AsO_4 solution. Compare the concentrations with those of the analogous species in 0.100 M H_3PO_4 solution. (See Example 18-17 and Table 18-7.)
59. Citric acid, the acid in lemons and other citrus fruits, has the structure



which we may abbreviate as $\text{C}_3\text{H}_5\text{O}(\text{COOH})_3$ or H_3A . It is a triprotic acid. Write the chemical equations for the three stages in the ionization of citric acid with the appropriate K_a expressions.



Charles D. Winters

60. Calculate the concentrations of H_3O^+ , OH^- , HSeO_4^- , and SeO_4^{2-} in 0.15 M H_2SeO_4 , selenic acid, solution.
61. Some kidney stones are crystalline deposits of calcium oxalate, a salt of oxalic acid, $(\text{COOH})_2$. Calculate the concentrations of H_3O^+ , OH^- , COOCOOH^- , and $(\text{COO}^-)_2$ in 0.12 M $(\text{COOH})_2$. Compare the concentrations with those obtained in Exercise 60. How can you explain the difference between the concentrations of HSeO_4^- and COOCOOH^- ? between SeO_4^{2-} and $(\text{COO}^-)_2$?
62. Rust stains can be removed from painted surfaces with a solution of oxalic acid, $(\text{COOH})_2$. Calculate the pH of a 0.045 M oxalic acid solution.
63. Calculate the pH and pOH of a carbonated soft drink that is 0.0035 M carbonic acid solution. Assume that there are no other acidic or basic components.



Charles D. Winters

Hydrolysis

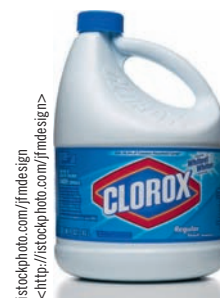
64. Define and illustrate the following terms clearly and concisely: (a) solvolysis; (b) hydrolysis.
65. Some anions, when dissolved, undergo no significant reaction with water molecules. What is the relative base strength of such an anion compared with water? What effect will dissolution of such anions have on the pH of the solution?
66. Some cations in aqueous solution undergo no significant reactions with water molecules. What is the relative acid strength of such a cation compared with water? What effect will dissolution of such cations have on the pH of the solution?
67. How can salts be classified conveniently into four classes? For each class, write the name and formula of a salt that fits into that category. Use examples other than those used in illustrations in this chapter.

Salts of Strong Bases and Strong Acids

68. What determines whether the aqueous solution of a salt is acidic, basic, or neutral?
69. Why do salts of strong bases and strong acids give neutral aqueous solutions? Use KNO_3 to illustrate. Write names and formulas for three other salts of strong bases and strong acids.
70. Which of the following are salts of a strong base and a strong acid? (a) Na_3PO_4 ; (b) K_2CO_3 ; (c) LiF ; (d) BaSO_4 ; (e) NaClO_3 .
71. Which of the following are salts of a strong base and a strong acid? (a) $\text{Ba}_3(\text{PO}_4)_2$; (b) LiNO_3 ; (c) NaI ; (d) CaCO_3 ; (e) KClO_4 .

Salts of Strong Bases and Weak Acids

72. Why do salts of strong bases and weak acids give basic aqueous solutions? Use sodium hypochlorite, NaOCl , to illustrate. (Clorox and some other commercial "chlorine bleaches" are 6% NaOCl .)



istockphoto.com/f/mdesign
<http://istockphoto.com/f/mdesign>

73. Some anions react with water to upset the $\text{H}_3\text{O}^+/\text{OH}^-$ balance. What is the relative base strength of such an anion compared with water? What effect will dissolution of such anions have on the pH of the solution?
74. Calculate the equilibrium constant for the reaction of azide ions, N_3^- , with water.



75. Write names and formulas for three salts of strong bases and weak acids other than those that appear in Section 18-8.
76. Calculate hydrolysis constants for the following anions of weak acids: (a) NO_2^- ; (b) OBr^- ; (c) HCOO^- . What is the relationship between K_a , the ionization constant for a weak acid, and K_b , the hydrolysis constant for the anion of the weak acid? (See Appendix F.)
77. Calculate the equilibrium constant for the reaction of hypiodite ions (OI^-) with water.
78. Calculate the pH of 1.5 *M* solutions of the following salts: (a) NaCH_3COO ; (b) KOBBr ; (c) LiCN .
79. Calculate the pH of 0.75 *M* solutions of the following salts: (a) NaNO_2 ; (b) NaOCl ; (c) NaHCOO .
80. (a) What is the pH of a 0.18 *M* solution of KOI ? (b) What is the pH of a 0.18 *M* solution of KF ?

Salts of Weak Bases and Strong Acids

81.  Why do salts of weak bases and strong acids give acidic aqueous solutions? Illustrate with NH_4NO_3 , a common fertilizer.
82. Write names and formulas for four salts of weak bases and strong acids.
83. Use values found in Table 18-6 and in Appendix G to calculate hydrolysis constants for the following cations of weak bases: (a) NH_4^+ ; (b) CH_3NH_3^+ , methylammonium ion; (c) $\text{C}_6\text{H}_5\text{NH}_3^+$, anilinium ion.
84. Use the values found in Table 18-6 and Appendix G to calculate hydrolysis constants for the following cations of weak bases: (a) $(\text{CH}_3)_2\text{NH}_2^+$, dimethylammonium ion; (b) $\text{C}_5\text{H}_5\text{NH}^+$, pyridinium ion; (c) $(\text{CH}_3)_3\text{NH}^+$, trimethylammonium ion.
85. Make a general statement relating parent base strength and extent of hydrolysis of the cations of Exercise 83 by using hydrolysis constants calculated in that exercise?
86. Calculate the pH of 0.26 *M* solutions of (a) NH_4NO_3 , (b) $\text{CH}_3\text{NH}_3\text{NO}_3$, (c) $\text{C}_6\text{H}_5\text{NH}_3\text{NO}_3$.

Salts of Weak Bases and Weak Acids

87.  Why are some aqueous solutions of salts of weak acids and weak bases neutral, whereas others are acidic and still others are basic?
88.  In each of the following question parts write the names and formulas for three salts of a weak acid and a weak base that give (a) neutral, (b) acidic, and (c) basic aqueous solutions.
89. If both the cation and anion of a salt react with water when dissolved, what determines whether the solution will be acidic, basic, or neutral? Classify aqueous solutions of the following salts as acidic, basic, or neutral: (a) $\text{NH}_4\text{F}(\text{aq})$; (b) $\text{CH}_3\text{NH}_3\text{OI}(\text{aq})$.

Salts That Contain Small, Highly Charged Cations

90. Choose the hydrated cations that react with water to give acidic solutions. (a) $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$; (b) $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$; (c) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$; (d) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. Write chemical equations for the reactions.
91. Why do some salts that contain cations related to insoluble bases (metal hydroxides) and anions related to strong acids give acidic aqueous solutions? Use $\text{Fe}(\text{NO}_3)_3$ to illustrate.
92. Calculate pH and percent hydrolysis for the following (see Table 18-10): (a) 0.15 *M* $\text{Al}(\text{NO}_3)_3$, aluminum nitrate; (b) 0.075 *M* $\text{Co}(\text{ClO}_4)_2$, cobalt(II) perchlorate; (c) 0.15 *M* MgCl_2 , magnesium chloride.
93.  Given pH values for solutions of the following concentrations, calculate hydrolysis constants for the hydrated cations: (a) 0.00050 *M* CeCl_3 , cerium(III) chloride, pH = 5.99; (b) 0.10 *M* $\text{Cu}(\text{NO}_3)_2$, copper(II) nitrate, pH = 4.50; (c) 0.10 *M* $\text{Sc}(\text{ClO}_4)_3$, scandium perchlorate, pH = 3.44.

Mixed Exercises

94. A weak acid, HA, has a $\text{p}K_a = 5.35$. What is the concentration of the anion, A^- , in a 0.100 *M* solution?
95. Calculate the pH of the following solutions. (a) 0.0070 *M* $\text{Ca}(\text{OH})_2$; (b) 0.25 *M* chloroacetic acid, ClCH_2COOH , $K_a = 1.4 \times 10^{-3}$; (c) 0.055 *M* pyridine, $\text{C}_5\text{H}_5\text{N}$.
96.  Classify aqueous solutions of the following salts as acidic, basic, or essentially neutral. Justify your choice. (a) $(\text{NH}_4)\text{HSO}_4$; (b) $(\text{NH}_4)_2\text{SO}_4$; (c) LiCl ; (d) LiBrO ; (e) AlCl_3 .
97. Repeat Exercise 96 for (a) Na_2SO_4 , (b) NH_4Cl , (c) KCl , (d) NH_4CN . (See Appendix F.)
98.  In aqueous solution some cations react with water to upset the $\text{H}_3\text{O}^+/\text{OH}^-$ balance. What is the relative acid strength of such a cation compared with water? What effect will dissolution of these cations have on the pH of the solution?
99.  Some plants require acidic soils for healthy growth. Which of the following could be added to the soil around such plants to increase the acidity of the soil? Write equations to justify your answers. (a) FeSO_4 ; (b) Na_2SO_4 ; (c) $\text{Al}_2(\text{SO}_4)_3$; (d) $\text{Fe}_2(\text{SO}_4)_3$; (e) BaSO_4 . Arrange the salts that give acidic solutions in order of increasing acidity. (Assume equal molarities of the salt solutions.)
100.  Some of the following salts are used in detergents and other cleaning materials because they produce basic solutions. Which of the following could *not* be used for this purpose? Write equations to justify your answers. (a) Na_2CO_3 ; (b) Na_2SO_4 ; (c) $(\text{NH}_4)_2\text{SO}_4$; (d) Na_3PO_4 .
101. Calculate the pH of each of the following solutions: (a) 0.038 g of barium hydroxide in 450. mL of solution, (b) 0.050 g of hydrogen iodide in 750. mL of solution, (c) 0.00075 g of HCl in 1.00 L of solution.
102. For each of the following pairs, tell which solution would have the lower pH. Tell how you arrive at each answer. (a) 0.015 *M* NH_4Br , ammonium bromide, and 0.015 *M* NH_4NO_3 , ammonium nitrate; (b) 0.015 *M* ammonium perchlorate, NH_4ClO_4 , and 0.010 *M* ammonium fluoride,

- NH₄F; (c) 0.010 M NH₄Cl and 0.050 M NH₄Cl. (*Hint*: Think before you calculate.)
103.  Arrange the following 0.1 M aqueous solutions in order of decreasing pH (highest to lowest).
Ba(NO₃)₂, HNO₃, NH₄NO₃, Al(NO₃)₃, NaOH
104.  Predict which base of each pair is the stronger base. Briefly explain how you arrived at your answer: (a) PH₃ or NH₃; (b) Br⁻ or F⁻; (c) ClO₃⁻ or ClO₂⁻; (d) HPO₄²⁻ or PO₄³⁻. (*Hint*: You may wish to review Chapter 10.)

Conceptual Exercises

105. How could we demonstrate that 0.012 M solutions of HCl and HNO₃ contain essentially no molecules of nonionized acid?
106. How could we demonstrate that 0.010 M solutions of HF and HNO₂ contain relatively few ions?
107. Carbonic acid, H₂CO₃, is diprotic and therefore has two ionization constants, $K_{a1} = 4.2 \times 10^{-7}$ and $K_{a2} = 4.8 \times 10^{-11}$. The pH of a carbonic acid solution can be calculated without using K_{a2} . Explain using a 0.100 M solution of carbonic acid.
108. Answer the following questions for 0.15 M solutions of the weak bases listed in Table 18-6. (a) In which solution is (i) the pH highest, (ii) the pH lowest, (iii) the pOH highest, (iv) the pOH lowest? (b) Which solution contains (i) the highest concentration of the cation of the weak base, (ii) the lowest concentration of the cation of the weak base?
109. Answer the following questions for 0.15 M solutions of the weak acids listed in Table 18-4. Which solution contains (a) the highest concentration of H₃O⁺, (b) the highest concentration of OH⁻, (c) the lowest concentration of H₃O⁺, (d) the lowest concentration of OH⁻, (e) the highest concentration of nonionized acid molecules, (f) the lowest concentration of nonionized acid molecules?
110. Write the balanced chemical equation for the ionization (or dissociation) that is believed to occur when each of the following compounds dissolves in water. Nitrous acid (HNO₂), barium hydroxide [Ba(OH)₂], hydrofluoric acid (HF), lithium hydroxide (LiOH), hydrocyanic acid (HCN), potassium hydroxide (KOH). Use a single arrow (→) to indicate a strong acid or strong base, one that ionizes completely (or to a very large extent), or a double arrow (⇌) to indicate a weak acid or weak base, one that ionizes partially (or to a small extent).
111. Listed below are five acids and their ionization constants. List their formulas in order of decreasing acid strength (i.e., strongest first).
benzoic acid (C₆H₅COOH), 6.3×10^{-5}
cyanic acid (HOCN), 3.5×10^{-4}
formic acid (HCOOH), 1.8×10^{-4}
hypobromous acid (HOBr), 2.5×10^{-9}
phenol (HC₆H₅O), 1.3×10^{-10}
112. "We have to get this problem of acid rain under control. We must do whatever it takes to get the pH down to zero!" Do you agree? Explain.

113. Of the following salts, which will produce an acidic solution? A neutral solution? A basic solution?
ammonium acetate (NH₄CH₃COO)
ammonium nitrate (NH₄NO₃)
ammonium sulfate [(NH₄)₂SO₄]
calcium sulfite (CaSO₃)
lithium hypochlorite (LiClO)
potassium chloride (KCl)

Building Your Knowledge

114. Ascorbic acid, C₅H₇O₄COOH, also known as vitamin C, is an essential vitamin for all mammals. Among mammals, only humans, monkeys, and guinea pigs cannot synthesize it in their bodies. K_a for ascorbic acid is 7.9×10^{-5} . Calculate [H₃O⁺] and pH in a 0.110 M solution of ascorbic acid.



Charles D. Winters

115. Arrange the following common kitchen samples from most acidic to most basic.
- | | |
|----------------------|---------------------------|
| carrot juice, pH 5.1 | blackberry juice, pH 3.4 |
| soap, pH 11.0 | red wine, pH 3.7 |
| egg white, pH 7.8 | milk of magnesia, pH 10.5 |
| sauerkraut, pH 3.5 | lime juice, pH 2.0 |
116.  The buildup of lactic acid in muscles causes pain during extreme physical exertion. The K_a for lactic acid, C₂H₅OCOOH, is 8.4×10^{-4} . Calculate the pH of a 0.110 M solution of lactic acid. Can you make a simplifying assumption in this case?
117. A 0.0100 molal solution of acetic acid freezes at -0.01938°C. Use this information to calculate the ionization constant for acetic acid. A 0.0100 molal solution is sufficiently dilute that it may be assumed to be 0.0100 molar without introducing a significant error.
118. The ion product for water, K_w , has the value 1.14×10^{-15} at 0.0 °C and 5.47×10^{-14} at 50. °C. Use the van't Hoff equation to estimate ΔH° for the ion product of water.

Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.



Molecular Reasoning exercises



More Challenging exercises

Blue-Numbered

exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

Use the *Handbook of Chemistry and Physics* or a suitable website to find answers to the following:

119. Find the approximate pH values of a number of foods, biological fluids, and so on. List the pH range of three foods or biological fluids found in this reference that are either not reported in the table in Section 18-3 of the textbook or have a different value reported in the table.
120. Locate the table of dissociation constants of organic acids in aqueous solutions and the table of dissociation constants of inorganic acids in aqueous solutions. In Section 18-5 of the textbook it is stated that for a polyprotic acid, “Successive ionization constants often decrease by a factor of approximately 10^4 to 10^6 , although some differences are outside this range.” Cite two inorganic examples that follow this rule of thumb. Cite one inorganic and two organic examples that are outside this range.
121. Nonmetal oxides are referred to as acid anhydrides. Use chemical equations to illustrate that via sequential reactions carbon dioxide added to water first hydrates and then dissociates to increase the acidity of the solution.
122. Use an internet search engine such as <http://www.google.com> to locate information about the medical condition achlorhydria. What acid and internal organ are involved? Does the normal presence of this acid explain one of the entries in the table “pH Range for a Few Common Substances” in Section 18-3?
123. Many medicines, vitamins, household cleaners, and lawn products contain acids and bases or their salts. Identify some of these products at your local supermarket. Are the acids and bases involved strong or weak? Some suggestions: Maalox®, Alka-Seltzer®.
124. Marble, a derivative of limestone (calcium carbonate), is often used for kitchen countertops. Marble countertops require extra care since they are easily etched by acidic substances such as lemon juice and vinegar. Write the unwanted chemical reaction between the marble and either vinegar or a generic acid.

Ionic Equilibria II: Buffers and Titration Curves

19



Anthocyanins are a general class of water-soluble pigments found in most plants. Every color but green has been recorded, with red, blue, and purple being the most common. Anthocyanins are natural indicators, as their colors vary with pH. Some plants can have different-colored flowers depending on the acidity of the soil they are grown in. Geraniums, for example, contain the anthocyanin pelargonin, which changes from orange-red (acidic) to blue (basic).

© Charles Volkland/AgeFotostock

OUTLINE

- 19-1** The Common Ion Effect and Buffer Solutions
- 19-2** Buffering Action
- 19-3** Preparation of Buffer Solutions
- 19-4** Acid–Base Indicators
- Titration Curves**
- 19-5** Strong Acid/Strong Base Titration Curves
- 19-6** Weak Acid/Strong Base Titration Curves
- 19-7** Weak Acid/Weak Base Titration Curves
- 19-8** Summary of Acid–Base Calculations

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Explain the common ion effect and give illustrations of its operation
- ▶ Recognize buffer solutions and describe their chemistry
- ▶ Describe how to prepare a buffer solution of a specified pH
- ▶ Carry out calculations related to buffer solutions and their action
- ▶ Explain what acid–base indicators are and how they function
- ▶ Describe what species are present at various stages of titration curves for (a) strong acids and strong bases, (b) weak acids and strong bases, and (c) weak acids and weak bases
- ▶ Carry out calculations based on titration curves for (a) strong acids and strong bases, and (b) weak acids and strong bases

In previous chapters, we calculated the acidity or basicity of separate aqueous solutions of strong acids, strong bases, weak acids, weak bases, and their salts. In this chapter, we will study (1) solutions that have both weak acids and weak bases present, (2) indicators, and (3) titration curves.

It can be a challenge to recognize the type of solution present. This can be even more difficult if the solution is formed by a partial or total neutralization reaction. To help you recognize the various solutions, a summary table (see Table 19-7) is included in Section 19-8. We encourage you to look at the table often as you progress through this chapter and as you review this and previous chapters.

19-1 The Common Ion Effect and Buffer Solutions

In laboratory reactions, in industrial processes, and in the bodies of plants and animals, it is often necessary to keep the pH nearly constant despite the addition of acids or bases. The oxygen-carrying capacity of the hemoglobin in your blood and the activity of the enzymes in your cells are very sensitive to the pH of your body fluids. A change in blood pH of 0.5 units (a change in $[\text{H}_3\text{O}^+]$ by a factor of about 3) can be fatal. Our bodies use a combination of compounds known as a *buffer system* to keep the pH within a narrow range.

The operation of a buffer solution depends on the *common ion effect*, a special case of LeChatelier's Principle.

When a solution of a weak electrolyte is altered by adding one of its ions from another source, the ionization of the weak electrolyte is suppressed. This behavior is termed the **common ion effect**.

Many types of solutions exhibit this behavior. Two of the most common kinds are

1. a solution of a weak acid plus a soluble ionic salt of the weak acid (e.g., CH_3COOH plus NaCH_3COO), and
2. a solution of a weak base plus a soluble ionic salt of the weak base (e.g., NH_3 plus NH_4Cl)

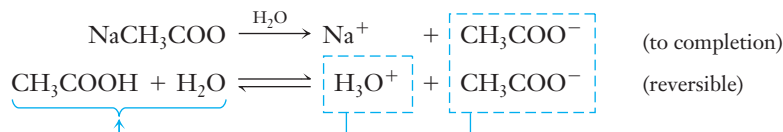
A **buffer solution** contains a conjugate acid–base pair with both the acid and base in reasonable concentrations. The conjugate acid–base pair must be of weak to moderate strength. Strong acids and bases do not make buffer solutions. The acidic component reacts with added strong bases. The basic component reacts with added strong acids.

- ▶ Buffer systems resist changes in pH.
- ▶ LeChatelier's Principle (Section 17-6) is applicable to equilibria in aqueous solution.

- ▶ You should review the discussion of conjugate acid–base pairs in Chapter 10 (Sections 10-4 and 10-5) and in Chapter 18 (Sections 18-6 to 18-10).

Weak Acids Plus Salts of Weak Acids

Consider a solution that contains acetic acid *and* sodium acetate, a soluble ionic salt of CH_3COOH . The NaCH_3COO is completely dissociated into its constituent ions, but CH_3COOH is only slightly ionized.



Both CH_3COOH and NaCH_3COO are sources of CH_3COO^- ions. The NaCH_3COO is soluble, so it is completely dissociated and provides a high $[\text{CH}_3\text{COO}^-]$. This shifts the ionization equilibrium of CH_3COOH far to the left, as CH_3COO^- combines with H_3O^+ to form nonionized CH_3COOH and H_2O . The result is a drastic decrease in $[\text{H}_3\text{O}^+]$ in the solution (higher pH).

Solutions that contain a weak acid plus a soluble salt of that weak acid are always less acidic than solutions that contain the same concentration of the weak acid alone.

In Example 18-11, we found that the H_3O^+ concentration in 0.10 M CH_3COOH is 1.3×10^{-3} mol/L (pH = 2.89). In Example 19-1, we will calculate the acidity of the same 0.10 M CH_3COOH solution after it is also made to be 0.20 M in the salt NaCH_3COO .

EXAMPLE 19-1 Weak Acid/Salt of Weak Acid Buffer Solution

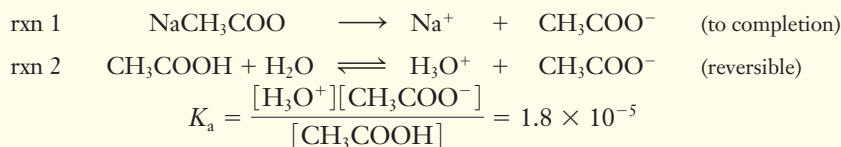
Calculate the concentration of H_3O^+ and the pH of a buffer solution that is 0.10 M in CH_3COOH and 0.20 M in NaCH_3COO .

Plan

Write the appropriate equations for *both* NaCH_3COO *and* CH_3COOH and the ionization constant expression for CH_3COOH . Then represent the *equilibrium* concentrations algebraically and substitute into the K_a expression.

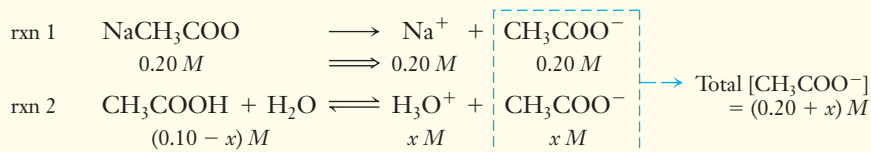
Solution

The appropriate equations and ionization constant expression are



This K_a expression is valid *for all solutions* that contain CH_3COOH . In a solution that contains both CH_3COOH and NaCH_3COO , the CH_3COO^- ions come from two sources. The ionization constant must be satisfied by the *total* CH_3COO^- concentration.

Because NaCH_3COO is completely dissociated, the $[\text{CH}_3\text{COO}^-]$ *from* NaCH_3COO will be 0.20 mol/L. Let $x = [\text{CH}_3\text{COOH}]$ that ionizes; then x is also equal to $[\text{H}_3\text{O}^+]$ and equal to $[\text{CH}_3\text{COO}^-]$ *from* CH_3COOH . The *total* concentration of CH_3COO^- is $(0.20 + x)$ M. The concentration of nonionized CH_3COOH is $(0.10 - x)$ M.

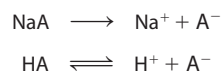


STOP & THINK

A solution of a *strong* acid and its salt (e.g., HCl/NaCl) has the acid nearly completely ionized, so the strong acid cannot be present in significant amounts. Therefore such a solution does not exhibit the common ion effect, nor can it act as a buffer solution. A similar reasoning applies to a solution of a *strong* base and its salt (e.g., NaOH/NaCl).

► This is an example of the common ion effect.

► We can represent these reactions with the abbreviated equations



STOP & THINK

We are adding the variable x to a quantity 0.20 that is more than two orders of magnitude greater than the K value, 1.8×10^{-5} , so it is safe to neglect x in the term $(0.20 + x)$. Similar reasoning lets us neglect x in the term $(0.10 - x)$. Review the Problem-Solving Tip "Simplifying Quadratic Equations" in Section 18-4.

► You can verify the validity of the assumptions by substituting the value $x = 9.0 \times 10^{-6}$ into the original K_a expression.

Substitution into the ionization constant expression for CH_3COOH gives

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(0.20 + x)}{0.10 - x} = 1.8 \times 10^{-5}$$

The small value of K_a suggests that x is very small. This leads to two assumptions. It is reasonable to assume (1) that x (from the ionization of CH_3COOH) is small because CH_3COOH is a weak acid (rxn 2), and (2) that its ionization is further suppressed by the high concentration of CH_3COO^- formed by the soluble salt, NaCH_3COO (rxn 1).

Assumption	Implication
$x \ll 0.20$, so $(0.20 + x) \approx 0.20$	Nearly all of the CH_3COO^- comes from NaCH_3COO (rxn 1) and very little CH_3COO^- comes from ionization of CH_3COOH (rxn 2)
$x \ll 0.10$, so $(0.10 - x) \approx 0.10$	Very little of the CH_3COOH ionizes (rxn 2)

Introducing these assumptions gives

$$\frac{0.20x}{0.10} = 1.8 \times 10^{-5} \quad \text{so} \quad x = 9.0 \times 10^{-6}$$

$$x M = [\text{H}_3\text{O}^+] = 9.0 \times 10^{-6} M \quad \text{so} \quad \text{pH} = 5.05$$

This can be compared to 0.10 M acetic acid, with $\text{pH} = 2.89$. The addition of the acetate anion, which is the conjugate base of acetic acid, raises the pH as one should qualitatively predict from acid–base reactions and the common ion effect (LeChatelier's Principle).

You should now work Exercise 10.

Let's calculate the percent ionization in the solution of Example 19-1.

$$\begin{aligned} \% \text{ ionization} &= \frac{[\text{CH}_3\text{COOH}]_{\text{ionized}}}{[\text{CH}_3\text{COOH}]_{\text{initial}}} \times 100\% \\ &= \frac{9.0 \times 10^{-6} M}{0.10 M} \times 100\% = 0.0090\% \text{ ionized} \end{aligned}$$

This compares with 1.3% ionization in 0.10 M CH_3COOH (see Example 18-11). Table 19-1 compares these solutions. The third column shows that $[\text{H}_3\text{O}^+]$ is *140 times greater* in 0.10 M CH_3COOH than in the solution to which 0.20 mol/L NaCH_3COO has been added. This is due to the common ion effect.

The calculation of the pH of any solution containing significant amounts of both a weak acid and a salt of that weak acid may be carried out as we have done in Example 19-1.

Table 19-1 Comparison of $[\text{H}_3\text{O}^+]$ and pH in Acetic Acid and Sodium Acetate–Acetic Acid Solutions

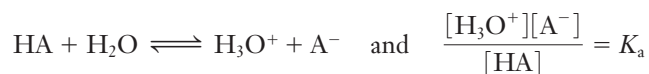
Solution	% CH_3COOH Ionized	$[\text{H}_3\text{O}^+]$	pH
0.10 M CH_3COOH	1.3%	$1.3 \times 10^{-3} M$	2.89
0.10 M CH_3COOH and 0.20 M NaCH_3COO	0.0090%	$9.0 \times 10^{-6} M$	5.05
$\Delta\text{pH} = 2.16$			



The two solutions of Table 19-1 in the presence of a universal indicator. The CH_3COOH solution is on the left.

Unless otherwise noted, all content on this page is © Cengage Learning.

Alternatively, we may proceed as follows. We start by writing the equations for the ionization of the *weak monoprotic acid* and its K_a as we did previously.



► HA and A^- represent the weak acid and its conjugate base, respectively.

Solving this expression for $[\text{H}_3\text{O}^+]$ gives

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

Consider a solution in which the weak acid and its anion (from an added salt) are both present at reasonable concentrations, such as greater than 0.050 *M*. Under these conditions, the concentration of the anion, $[\text{A}^-]$, in the solution can be assumed to be entirely due to the dissolved salt. With these restrictions, the preceding expression becomes

► These are the kinds of assumptions we made in Example 19-1.

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{conjugate base}]}$$

$[\text{HA}]$ is the concentration of nonionized weak acid (in most cases, this is the total acid concentration), and $[\text{conjugate base}]$ is the concentration of the anion from the dissolved salt.

Taking the logarithm of both sides of the preceding equation, we obtain

$$\log [\text{H}_3\text{O}^+] = \log K_a + \log \frac{[\text{acid}]}{[\text{conjugate base}]}$$

Multiplying by -1 gives

$$-\log [\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{acid}]}{[\text{conjugate base}]}$$

Recall that in Chapter 18 we defined $-\log [\text{H}_3\text{O}^+]$ (or $-\log [\text{H}^+]$) as pH and $-\log K_a$ as $\text{p}K_a$. The preceding equation can then be written as

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base (salt)}]}{[\text{acid}]} \quad (\text{for acid/salt buffer})$$

► Remember that
 $-\log x = \log \frac{1}{x}$

This equation is known as the **Henderson–Hasselbalch equation**. Workers in the biological sciences use it frequently. Because the amount of weak acid dissociated is very small, the values for $[\text{conjugate base}]$ and $[\text{acid}]$ are essentially their initial concentrations after mixing, ignoring the negligible reaction that they then undergo.

EXAMPLE 19-2 Weak Acid/Salt of Weak Acid Buffer Solution (via the Henderson–Hasselbalch Equation)

Use the Henderson–Hasselbalch equation to calculate the pH of the buffer solution in Example 19-1.

Plan

The Henderson–Hasselbalch equation is $\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$. The value for $\text{p}K_a$ for acetic acid can be calculated from the value of K_a found in Example 19-1 and many other places. The solution in Example 19-1 is 0.10 *M* in CH_3COOH and 0.20 *M* in NaCH_3COO . The values used for $[\text{conjugate base}]$ and $[\text{acid}]$ are their initial concentrations after mixing but before reaction.

STOP & THINK

For this example:

conjugate base = CH_3COO^-
 = NaCH_3COO
 = sodium acetate
 = salt of weak acid

Solution

The appropriate values needed for the Henderson-Hasselbalch equation are

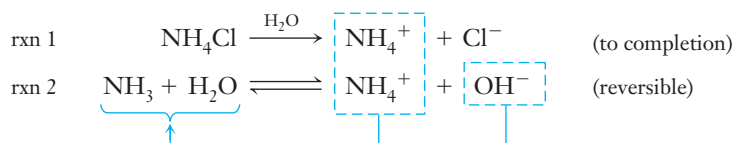
$$\begin{aligned} \text{p}K_{\text{a}} &= -\log K_{\text{a}} = -\log 1.8 \times 10^{-5} = 4.74 \\ [\text{conjugate base}] &= [\text{CH}_3\text{COO}^-] = [\text{NaCH}_3\text{COO}]_{\text{initial}} = 0.20 \text{ M} \\ [\text{acid}] &= [\text{CH}_3\text{COOH}]_{\text{initial}} = 0.10 \text{ M} \\ \text{pH} &= \text{p}K_{\text{a}} + \log \frac{[\text{conjugate base}]}{[\text{acid}]} = 4.74 + \log \frac{0.20}{0.10} \\ &= 4.74 + \log 2.0 = 4.74 + 0.30 = 5.04 \end{aligned}$$

► The values $\text{p}K_{\text{a}} = 4.74$, $\log 2.0$, and $\text{pH} = 5.04$ all have two significant figures.

You should now work Exercise 11.

Weak Bases Plus Salts of Weak Bases

Let us now consider the second common kind of buffer solution, containing a weak base and its salt. A solution that contains aqueous NH_3 and ammonium chloride, NH_4Cl , a soluble ionic salt of NH_3 , is typical. The NH_4Cl is completely dissociated, but aqueous NH_3 is only slightly ionized.



Both NH_4Cl and aqueous NH_3 are sources of NH_4^+ ions. The soluble, completely dissociated NH_4Cl provides a high $[\text{NH}_4^+]$. This shifts the ionization equilibrium of aqueous NH_3 far to the left, as NH_4^+ ions combine with OH^- ions to form nonionized NH_3 and H_2O . The result is that $[\text{OH}^-]$ is decreased significantly.

Solutions that contain a weak base plus a soluble salt of that weak base are always less basic than solutions that contain the same concentration of the weak base alone.

EXAMPLE 19-3 Weak Base/Salt of Weak Base Buffer Solution

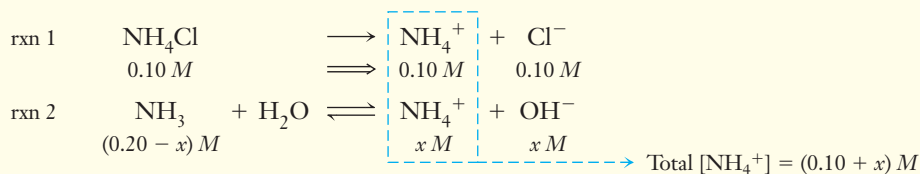
Calculate the concentration of OH^- and the pH of a solution that is 0.20 M in aqueous NH_3 and 0.10 M in NH_4Cl .

Plan

Write the appropriate equations for *both* NH_4Cl and NH_3 and the ionization constant expression for NH_3 . Then represent the *equilibrium* concentrations algebraically and substitute into the K_{b} expression.

Solution

The appropriate equations and algebraic representations of concentrations are



Substitution into the K_b expression for aqueous NH_3 gives

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(0.10 + x)(x)}{0.20 - x}$$

The small value of K_b suggests that x is very small. This leads to two assumptions. It is reasonable to assume (1) that x (from the ionization of NH_3) is small because NH_3 is a weak base (rxn 2), and (2) that its ionization is further suppressed by the high concentration of NH_4^+ formed by the soluble salt, NH_4Cl (rxn 1).

Assumption	Implication
$x \ll 0.10$, so $(0.10 + x) \approx 0.10$	Nearly all of the NH_4^+ comes from NH_4Cl (rxn 1), and very little NH_4^+ comes from ionization of NH_3 (rxn 2)
$x \ll 0.20$, so $(0.20 - x) \approx 0.20$	Very little of the NH_3 ionizes (rxn 2)

Introducing these assumptions gives

$$\frac{0.10x}{0.20} = 1.8 \times 10^{-5} M \quad \text{so} \quad x = 3.6 \times 10^{-5} M$$

$$x M = [\text{OH}^-] = 3.6 \times 10^{-5} M \quad \text{so} \quad \text{pOH} = 4.44 \quad \text{and} \quad \text{pH} = 14 - \text{pOH} = 9.56$$

You should now work Exercise 12.

STOP & THINK

The two-orders-of-magnitude guideline introduced in Chapter 18 suggests these assumptions. But we can *never* neglect the variable x when it stands alone as a multiplier! Adding or subtracting a very small number sometimes makes little difference in the result, but multiplying or dividing by a small number is always important!

► The percent ionization of NH_3 in this solution is

$$\frac{3.6 \times 10^{-5} M_{\text{ionized}}}{0.20 M_{\text{original}}} \times 100\% = 0.018\%$$

In Example 18-15 we calculated $[\text{OH}^-]$ and pH for 0.20 M aqueous NH_3 . Compare those results with the values obtained in Example 19-3 (Table 19-2). The concentration of OH^- is *53 times greater* in the solution containing only 0.20 M aqueous NH_3 than in the solution to which 0.10 mol/L NH_4Cl has been added. This is another demonstration of the common ion effect.

Table 19-2 Comparison of $[\text{OH}^-]$ and pH in Ammonia and Ammonium Chloride–Ammonia Solutions

Solution	% NH ₃ Ionized	[OH ⁻]	pH	
0.20 M aq NH ₃	0.95%	$1.9 \times 10^{-3} M$	11.28	} ΔpH = -1.72
0.20 M aq NH ₃ and	0.018%	$3.6 \times 10^{-5} M$	9.56	
0.10 M aq NH ₄ Cl				

We can derive a relationship for $[\text{OH}^-]$ in a solution containing a weak base, B, *plus* a salt that contains the cation, BH^+ , of the weak base, just as we did for weak acids. In general terms the equation for the ionization of a monobasic weak base and its K_b expression are



Solving the K_b expression for $[\text{OH}^-]$ gives

$$[\text{OH}^-] = K_b \times \frac{[\text{B}]}{[\text{BH}^+]}$$

Taking the logarithm of both sides of the equation gives

$$\log[\text{OH}^-] = \log K_b + \log \frac{[\text{B}]}{[\text{BH}^+]}$$



The two solutions in Table 19-2 in the presence of a universal indicator. The NH_3 solution is on the left. Can you calculate the percentage of NH_3 that is ionized in these two solutions?

► B and BH^+ represent the weak base and its conjugate acid, respectively—for example, NH_3 and NH_4^+ .

Multiplying by -1 , substituting pK_b for $-\log K_b$ and rearranging gives another form of the *Henderson–Hasselbalch equation* for solutions containing a weak base plus a salt of the weak base.

$$pOH = pK_b + \log \frac{[BH^+]}{[B]} \quad (\text{for base/salt buffer})$$

The Henderson–Hasselbalch equation is valid for solutions of weak bases plus salts of weak bases with univalent anions in reasonable concentrations. In general terms we can also write this equation as

$$pOH = pK_b + \log \frac{[\text{conjugate acid (salt)}]}{[\text{base}]} \quad (\text{for base/salt buffer})$$

► You should solve Example 19-3 using this base/salt form of the Henderson–Hasselbalch equation.

19-2 Buffering Action

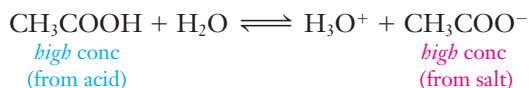
A buffer solution is able to react with either H_3O^+ or OH^- ions, whichever is added, to keep the pH approximately the same.

Thus, a buffer solution resists changes in pH. When we add a modest amount of a strong base or a strong acid to a buffer solution, the pH changes very little. More concentrated buffer solutions can react with larger amounts of added acid or base before significant pH changes occur.

The two common kinds of buffer solutions are the ones we have just discussed—namely, solutions containing (1) a weak acid plus a soluble ionic salt of the weak acid and (2) a weak base plus a soluble ionic salt of the weak base.

Solutions of a Weak Acid and a Salt of the Weak Acid

A solution containing acetic acid, CH_3COOH , and sodium acetate, $NaCH_3COO$, is an example of this kind of buffer solution. The acidic component is CH_3COOH . The basic component is $NaCH_3COO$ because the CH_3COO^- ion is the conjugate base of CH_3COOH . The operation of this buffer depends on the equilibrium



If we add a modest amount of a strong acid such as HCl to this solution, it produces H_3O^+ . As a result of the added H_3O^+ , the reaction shifts to the *left* as predicted by LeChatelier's Principle, to use up most of the added H_3O^+ and reestablish equilibrium. Because the $[CH_3COO^-]$ in the buffer solution is high, this can occur to a great extent. The net reaction is



or, written as a formula unit equation,



This reaction goes nearly to completion because CH_3COOH is a *weaker* acid than HCl ; even when mixed from separate sources, its ions have a strong tendency to form nonionized CH_3COOH molecules rather than remain separate.

When a modest amount of a strong base, such as $NaOH$, is added to the CH_3COOH – $NaCH_3COO$ buffer solution, some of the OH^- can react directly with the acetic acid, CH_3COOH , which is present in a large amount. Additional OH^- can react with the rela-



Maria G. Clarke

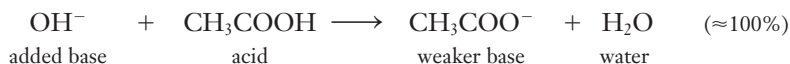
Three common examples of buffers. Many medications are buffered to minimize digestive upset. Most body fluids, including blood plasma, contain very efficient natural buffer systems. Buffer capsules are used in laboratories to prepare solutions of specified pH.

► The net effect is to neutralize most of the H_3O^+ from HCl by forming nonionized CH_3COOH molecules. This slightly decreases the ratio $[CH_3COO^-]/[CH_3COOH]$, which governs the pH of the solution.

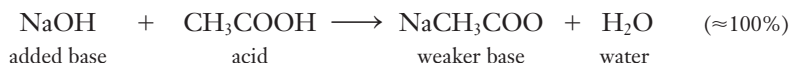
tively small amount of H_3O^+ present, greatly reducing $[\text{H}_3\text{O}^+]$. This disturbs the CH_3COOH ionization equilibrium.



This equilibrium then shifts to the *right* to replace some of the depleted H_3O^+ . Because the $[\text{CH}_3\text{COOH}]$ is high, this can occur to a great extent. The net result is the neutralization of most of the added OH^- .



or, written as a formula unit equation,



► The net effect is to neutralize most of the OH^- from NaOH. This *slightly* increases the ratio $[\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}]$, which governs the pH of the solution.

EXAMPLE 19-4 Buffering Action

We add 0.010 mol of solid NaOH to 1.00 liter of a buffer solution that is 0.100 M in CH_3COOH and 0.100 M in NaCH_3COO . How much will $[\text{H}_3\text{O}^+]$ and pH change? Assume that there is no volume change due to the addition of solid NaOH.

Plan

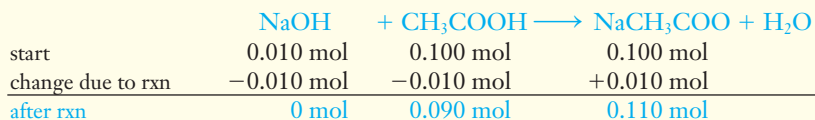
Calculate $[\text{H}_3\text{O}^+]$ and pH for the original buffer solution. Then write the reaction summary that shows how much of the CH_3COOH is neutralized by NaOH (forming additional NaCH_3COO). Calculate $[\text{H}_3\text{O}^+]$ and pH for the resulting new buffer solution. Finally, calculate the change in pH.

Solution

For the 0.100 M CH_3COOH and 0.100 M NaCH_3COO buffer solution, we can write

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} = 1.8 \times 10^{-5} \times \frac{0.100}{0.100} = 1.8 \times 10^{-5} \text{ M}; \text{pH} = 4.74$$

When solid NaOH is added, it reacts with CH_3COOH to form more NaCH_3COO .



The volume of the solution is still 1.00 liter, so we now have a buffer solution that is 0.090 M in CH_3COOH and 0.110 M in NaCH_3COO . In this solution,

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} = 1.8 \times 10^{-5} \times \frac{0.090}{0.110} = 1.5 \times 10^{-5} \text{ M}; \text{pH} = 4.82$$

The addition of 0.010 mol of solid NaOH to 1.00 liter of this buffer solution decreases $[\text{H}_3\text{O}^+]$ from $1.8 \times 10^{-5} \text{ M}$ to $1.5 \times 10^{-5} \text{ M}$ and increases pH from 4.74 to 4.82, a change of 0.08 pH unit, which is a very slight change. This is a change in $[\text{OH}^-]$ by a factor of only 1.2, from 5.5×10^{-10} to 6.6×10^{-10} , or a change of only 20%.

You should now work Exercise 24.

► We could have used the Henderson–Hasselbalch equation to solve for both pH values in this example.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

The $[\text{H}_3\text{O}^+]$ can then be obtained from the pH value.

► This is enough NaOH to neutralize 10% of the acid.

To emphasize the effectiveness of such a buffer solution, let's describe what happens when we add 0.010 mole of solid NaOH to one liter of 0.100 M CH_3COOH ($\text{pH} = 2.89$) to give a solution that is 0.090 M in CH_3COOH and 0.010 M in NaCH_3COO . The pH of the solution is 3.79, which is only 0.90 pH unit higher than that of the 0.100 M CH_3COOH solution.

By contrast, adding 0.010 mole of NaOH to enough pure H_2O to give one liter produces a 0.010 M solution of NaOH: $[\text{OH}^-] = 1.0 \times 10^{-2} \text{ M}$ and $\text{pOH} = 2.00$. The pH of this solution is 12.00, an increase of 5.00 pH units above that of pure H_2O . This corresponds to decreasing $[\text{H}_3\text{O}^+]$ (and increasing $[\text{OH}^-]$) by a factor of 10^5 , or 100,000.

► $\text{pH} + \text{pOH} = 14$



The pH of blood is controlled by naturally occurring buffers in the blood.

Table 19-3 Changes in pH Caused by Addition of Pure Base or Acid to One Liter of Solution

We Have 1.00 L of Original Solution	When We Add 0.010 mol NaOH(s)		When We Add 0.010 mol HCl(g)	
	pH changes by	$[\text{H}_3\text{O}^+]$ decreases by a factor of	pH changes by	$[\text{H}_3\text{O}^+]$ increases by a factor of
buffer solution (0.10 M NaCH_3COO and 0.10 M CH_3COOH)	+0.08 pH unit	1.2	−0.08 pH unit	1.2
0.10 M CH_3COOH	+0.90	7.9	−0.89	7.8
pure H_2O	+5.00	100,000	−5.00	100,000

In summary, 0.010 mole of NaOH

added to 1.00 L of the $\text{CH}_3\text{COOH}/\text{NaCH}_3\text{COO}$ buffer, pH 4.74 $\longrightarrow$ 4.82

added to 1.00 L of 0.100 M CH_3COOH , pH 2.89 $\longrightarrow$ 3.78

added to 1.00 L of pure H_2O , pH 7.00 $\longrightarrow$ 12.00

In similar fashion we could calculate the effects of adding 0.010 mole of pure HCl(g) instead of pure NaOH to 1.00 liter of each of these three solutions. This would result in the following changes in pH:

added to 1.00 L of the $\text{CH}_3\text{COOH}/\text{NaCH}_3\text{COO}$ buffer, pH 4.74 $\longrightarrow$ 4.66

added to 1.00 L of 0.100 M CH_3COOH , pH 2.89 $\longrightarrow$ 2.00

added to 1.00 L of pure H_2O , pH 7.00 $\longrightarrow$ 2.00

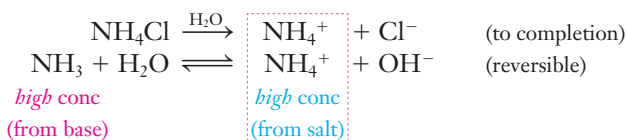
The results of adding NaOH or HCl to these solutions (Table 19-3) demonstrate the efficiency of the buffer solution. We recall that each change of 1 pH unit means that the $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ change by a factor of 10. In these terms, the effectiveness of the buffer solution in controlling pH is even more dramatic.

STOP & THINK

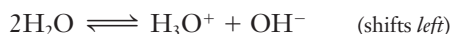
When a little strong acid is added to a solution of a weak acid, the $[\text{H}_3\text{O}^+]$ from the weak acid is negligible compared to the $[\text{H}_3\text{O}^+]$ from the strong acid.

Solutions of a Weak Base and a Salt of the Weak Base

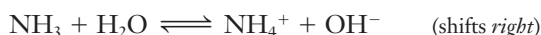
An example of this type of buffer solution is one that contains the weak base ammonia, NH_3 , and its soluble ionic salt ammonium chloride, NH_4Cl . The reactions responsible for the operation of this buffer are



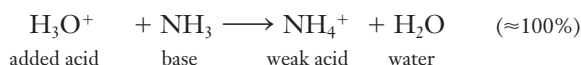
If a strong acid such as HCl is added to this buffer solution, the resulting H_3O^+ shifts the equilibrium reaction



strongly to the *left*. As a result of the diminished OH^- concentration, the reaction



shifts markedly to the *right*. Because the $[\text{NH}_3]$ in the buffer solution is high, this can occur to a great extent. The net reaction is



► The net effect is to neutralize most of the H_3O^+ from HCl. This slightly increases the ratio $[\text{NH}_4^+]/[\text{NH}_3]$, which governs the pH of the solution.

Unless otherwise noted, all content on this page is © Cengage Learning.

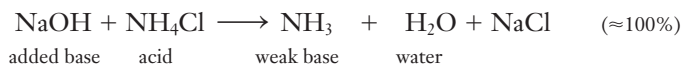
When a strong base such as NaOH is added to the *original* buffer solution, it is neutralized by the more acidic component, NH_4^+ (the conjugate acid of ammonia).



Because the $[\text{NH}_4^+]$ is high, this can occur to a great extent. The result is the neutralization of OH^- by NH_4^+ ,



or, as a formula unit equation,



► The net effect is to neutralize most of the OH^- from NaOH. This slightly decreases the ratio $[\text{NH}_4^+]/[\text{NH}_3]$, which governs the pH of the solution.

Summary Changes in pH are minimized in buffer solutions because the basic component can react with added H_3O^+ ions (producing additional weak acid), while the acidic component can react with added OH^- ions (producing additional weak base).

19-3 Preparation of Buffer Solutions

Buffer solutions can be prepared by mixing other solutions. When solutions are mixed, the volume in which each solute is contained increases, so solute concentrations change. These changes in concentration must be considered. If the solutions are dilute, we may assume that their volumes are additive.

Buffer Preparation by Mixing of a Conjugate Acid–Base Pair

EXAMPLE 19-5 pH of a Buffer Solution

Calculate the concentration of H_3O^+ and the pH of a buffer solution prepared by mixing 200. mL of 0.10 M NaF and 100. mL of 0.050 M HF. $K_a = 7.2 \times 10^{-4}$ for HF.

Plan

Calculate the number of millimoles (or moles) of NaF and HF and then the molarity of each solute in the solution after mixing. Write the appropriate equations for both NaF and HF, represent the equilibrium concentrations algebraically, and substitute into the K_a expression for HF.

Solution

When two dilute solutions are mixed, we assume that their volumes are additive. The volume of the new solution will be 300. mL. Mixing a solution of a weak acid with a solution of its salt does not form any new species (though it does change their concentrations). So we have a straightforward buffer calculation. We calculate the number of millimoles (or moles) of each compound and the molarities in the new solution.

$$\left. \begin{array}{l} \underline{\hspace{1cm}} \text{ mmol NaF} = 200. \text{ mL} \times \frac{0.10 \text{ mmol NaF}}{\text{mL}} = 20. \text{ mmol NaF} \\ \underline{\hspace{1cm}} \text{ mmol HF} = 100. \text{ mL} \times \frac{0.050 \text{ mmol HF}}{\text{mL}} = 5.0 \text{ mmol HF} \end{array} \right\} \text{ in } 300. \text{ mL}$$

The molarities of NaF and HF in the solution are

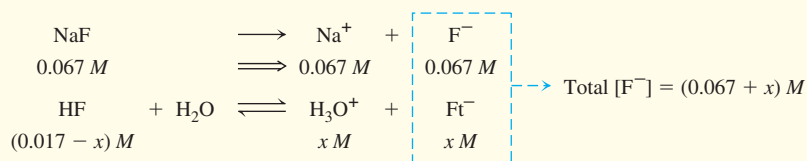
$$\frac{20. \text{ mmol NaF}}{300. \text{ mL}} = 0.067 \text{ M NaF} \quad \text{and} \quad \frac{5.0 \text{ mmol HF}}{300. \text{ mL}} = 0.017 \text{ M HF}$$

► Alternatively, we could substitute into the Henderson–Hasselbalch equation and solve for pH, and then convert to $[\text{H}_3\text{O}^+]$.

STOP & THINK

It is very important to remember to use the total solution volume of 300 mL for the calculations in this example!

The appropriate equations and algebraic representations of concentrations are



Substituting into the K_a expression for hydrofluoric acid gives

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(0.067 + x)}{(0.017 - x)} = 7.2 \times 10^{-4}$$

The two-orders-of-magnitude guideline suggests that x is negligible compared with 0.067 and 0.017 in this expression. (When in doubt, solve the equation using the simplifying assumption. Then decide whether the assumption was valid.) Assume that $(0.067 + x) \approx 0.067$ and $(0.017 - x) \approx 0.017$.

► Using the Henderson–Hasselbalch equation, we obtain:

$$\text{pH} = -\log(7.2 \times 10^{-4}) + \log \frac{0.067}{0.017}$$

$$\text{pH} = 3.14 + 0.596 = 3.74$$

$$\frac{0.067x}{0.017} = 7.2 \times 10^{-4} \quad ; \quad x = 1.8 \times 10^{-4}\text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 3.74 \text{ (Our assumption was valid)}$$

You should now work Exercise 36.

We often need a buffer solution of a desired pH. One way to prepare such a solution is to add a salt of a weak base (or weak acid) to a solution of the weak base (or weak acid).

EXAMPLE 19-6 Buffer Preparation by Addition of a Salt

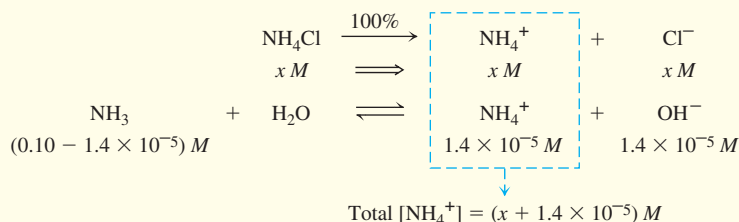
A solution is 0.10 M in aqueous NH_3 . Calculate (a) the number of moles and (b) the number of grams of NH_4Cl that must be added to 500 mL of this solution to prepare a buffer solution with $\text{pH} = 9.15$. You may neglect the volume change due to addition of solid NH_4Cl .

Plan

Convert the given pH to the desired $[\text{OH}^-]$ by the usual procedure. Write the appropriate equations for the reactions of NH_4Cl and NH_3 and represent the equilibrium concentrations. Then, substitute into the K_b expression, and solve for the concentration of NH_4Cl required. This allows calculation of the amount of solid NH_4Cl to be added.

Solution

- (a) Because the desired $\text{pH} = 9.15$, $\text{pOH} = 14.00 - 9.15 = 4.85$. So $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4.85} = 1.4 \times 10^{-5}\text{ M}$ OH^- desired. Let x mol/L be the necessary molarity of NH_4Cl . Because $[\text{OH}^-] = 1.4 \times 10^{-5}\text{ M}$, this must be the $[\text{OH}^-]$ produced by ionization of NH_3 . The equations and representations of equilibrium concentrations follow.



Substitution into the K_b expression for aqueous ammonia gives

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(x + 1.4 \times 10^{-5})(1.4 \times 10^{-5})}{(0.10 - 1.4 \times 10^{-5})}$$

NH_4Cl is 100% dissociated, so $x \gg 1.4 \times 10^{-5}$. Then $(x + 1.4 \times 10^{-5}) \approx x$.

$$\frac{(x)(1.4 \times 10^{-5})}{0.10} = 1.8 \times 10^{-5} \quad ; \quad x = 0.13 \text{ M} = [\text{NH}_4^+] = M_{\text{NH}_4\text{Cl}}$$

Now we calculate the number of moles of NH_4Cl that must be added to prepare 500. mL (0.500 L) of buffer solution.

$$\underline{\quad} \text{ mol NH}_4\text{Cl} = 0.500 \text{ L} \times \frac{0.13 \text{ mol NH}_4\text{Cl}}{\text{L}} = 0.065 \text{ mol NH}_4\text{Cl}$$

$$(b) \quad \underline{\quad} \text{ g NH}_4\text{Cl} = 0.065 \text{ mol} \times \frac{53.5 \text{ g NH}_4\text{Cl}}{\text{mol NH}_4\text{Cl}} = 3.5 \text{ g NH}_4\text{Cl}$$

You should now work Exercise 39.

STOP & THINK

Here x does *not* represent a *change* in concentration, but rather the initial concentration of NH_4Cl . We do *not* assume that $x \ll 1.4 \times 10^{-5}$, but rather the reverse.

► Example 19-6 can be solved using the base/salt form of the Henderson–Hasselbalch equation as follows:

$$\begin{aligned} \text{pOH} &= \text{p}K_b + \log \frac{[\text{conjugate acid}]}{[\text{base}]} \\ 4.85 &= -\log(1.8 \times 10^{-5}) \\ &\quad + \log \frac{[\text{conjugate acid}]}{[0.10]} \\ 4.85 &= 4.74 + \log[\text{conjugate acid}] - (-1.00) \\ [\text{conjugate acid}] &= 0.13 \text{ M} = [\text{NH}_4^+] \end{aligned}$$

A We add 3.5 grams of NH_4Cl to a 500-mL volumetric flask.

B We dissolve it in a little of the 0.10 M NH_3 solution.

C We then dilute to 500 mL with the 0.10 M NH_3 solution.

D When a universal indicator is added, the green color shows that the buffer solution has a lower pH than the original NH_3 solution (blue).

Preparation of the buffer solution in Example 19-6.

We have used K_a or K_b expressions or the Henderson–Hasselbalch equation in its acid/salt or base/salt form to find the pH of buffered solutions. Either of these calculations involves a *ratio* of concentrations, for instance $\frac{[\text{conjugate base}]}{[\text{acid}]}$. Although the ratios are written in terms of molarities, it is not always necessary to use concentrations in the calculations. Both reagents are present in a *single* buffer solution, so the solution volume cancels from the molarity ratio. For example:

$$\frac{[\text{conjugate base}]}{[\text{acid}]} = \frac{\frac{\text{mol conjugate base}}{\text{L soln}}}{\frac{\text{mol acid}}{\text{L soln}}} = \frac{\text{mol conjugate base}}{\text{mol acid}}$$

Thus we see that a molarity ratio in the acid/salt Henderson–Hasselbalch equation can be treated as a mole (or millimole) ratio. A similar conclusion can be reached for the base/salt version of the Henderson–Hasselbalch equation or for the K_a or K_b expressions that were used in previous buffer calculations.

Thus the Henderson–Hasselbalch equation for buffers can be written in the following forms:

$$\begin{aligned} \text{For an acid/salt buffer: } \text{pH} &= \text{p}K_a + \frac{\text{mol conjugate base}}{\text{mol acid}} = \text{p}K_a + \frac{\text{mmol conjugate base}}{\text{mmol acid}} \\ \text{For a base/salt buffer: } \text{pOH} &= \text{p}K_b + \frac{\text{mol conjugate acid}}{\text{mol base}} = \text{p}K_b + \frac{\text{mmol conjugate acid}}{\text{mmol base}} \end{aligned}$$

CHEMISTRY IN USE

Fun with Carbonates

Carbonates react with acids to produce carbon dioxide. This property of carbonates has been exploited in many ways, both serious and silly.

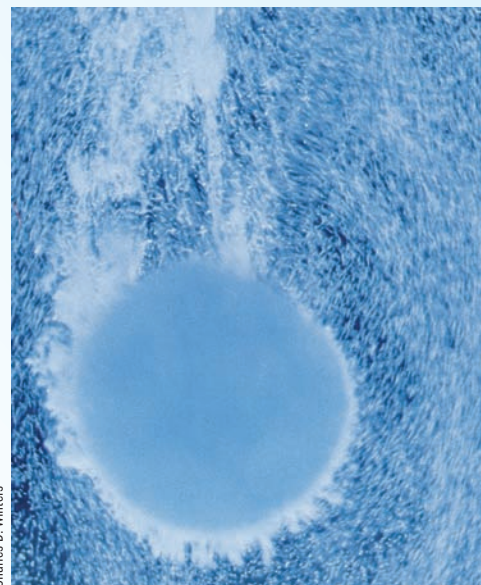
One of the giddiest applications of this behavior of carbonates is seen in Mad Dawg, a foaming bubble gum developed in the early 1990s. If you chew a piece of this gum, large quantities of foam are produced so that it is difficult to keep the colorful lather from oozing out of your mouth. The froth begins to form as your teeth mix saliva with the gum's ingredients (sodium hydrogen carbonate, citric acid, malic acid, food coloring, and flavoring).

How is this foam produced? When citric acid and malic acid dissolve in saliva, they produce hydrogen ions, which decompose the sodium hydrogen carbonate (baking soda) to produce carbon dioxide, a gas. These bubbles of carbon dioxide produce the foam. Large quantities of foam are produced because citric and malic acids taste sour, which stimulates salivation.

A common medical recipe for a similar combination of ingredients is found in Alka Seltzer tablets; these contain sodium hydrogen carbonate, citric acid, and aspirin. The acid and carbonate react in water to produce carbon dioxide, which gives the familiar fizz of Alka Seltzer.

Makeup artists add baking soda to cosmetics to produce monster-flesh makeup. When the hero throws acid (which is actually vinegar, a dilute solution of acetic acid) into the monster's face, the acetic acid reacts with sodium hydrogen carbonate to produce the disgustingly familiar scenes of "dissolving flesh" that we see in horror movies. The ability of baking soda to produce carbon dioxide delights children of all ages as it creates monsters in the movies.

Many early fire extinguishers utilized the reaction of sodium hydrogen carbonate with acids. A metal cylinder was filled with a solution of sodium hydrogen carbonate and water; a bottle filled with sulfuric acid was placed above the water layer. Invert-



Charles D. Winters

Alka Seltzer™

ing the extinguisher activated it by causing the acid to spill into the carbonate solution. The pressure produced by gaseous carbon dioxide gas pushed the liquid contents out through a small hose.

Kitchen oven fires can usually be extinguished by throwing baking soda onto the flame. When heated, carbonates decompose to produce carbon dioxide, which smothers fires by depriving them of oxygen.

Chefs frequently use the heat-sensitive nature of carbonates to test the freshness of a box of baking soda. Pouring some boiling water over a little fresh baking soda results in active bubbling. Less active bubbling means the baking soda is unlikely to work well in a baking recipe.

RONALD DELORENZO

Buffer Preparation by Partial Neutralization

In practice, a common method of preparing a buffer solution is by *partial* neutralization of a weak acid solution by adding a strong base solution. For example,



If an appreciable amount of the weak acid remains unneutralized, then this solution contains significant concentrations of a *weak acid* and *its conjugate base*, just as though we had added the salt from a separate solution; thus, it is a buffer solution. Example 19-7 illustrates the preparation of a buffer by this method.

EXAMPLE 19-7 Buffer Preparation by Partial Neutralization

Calculate the pH of a solution obtained by mixing 400. mL of a 0.200 *M* acetic acid solution and 100. mL of a 0.300 *M* sodium hydroxide solution.

Plan

Sodium hydroxide, NaOH, is a strong base, so it reacts with acetic acid, CH₃COOH, to form sodium acetate, NaCH₃COO. If an appreciable amount of excess acetic acid is still present after the sodium hydroxide has reacted, the excess acetic acid and the newly formed sodium acetate solution form a buffer solution.

Solution

We first calculate how much of the weak acid has been neutralized. The numbers of millimoles of CH₃COOH and NaOH mixed are calculated as

$$\text{mmol CH}_3\text{COOH} = (0.200 \text{ mmol/mL}) \times 400. \text{ mL} = 80.0 \text{ mmol}$$

$$\text{mmol NaOH} = (0.300 \text{ mmol/mL}) \times 100. \text{ mL} = 30.0 \text{ mmol}$$

Not enough NaOH is present to neutralize all of the CH₃COOH, so NaOH is the *limiting reactant*.

	NaOH	+ CH ₃ COOH	→	NaCH ₃ COO + H ₂ O	
start	30.0 mmol	80.0 mmol		0	—
change	−30.0 mmol	−30.0 mmol		+30.0 mmol	—
after rxn	0.0 mmol	50.0 mmol		30.0 mmol	

Because NaCH₃COO is a soluble salt, it provides 30.0 mmol CH₃COO[−] to the solution. This solution contains a significant amount of CH₃COOH not yet neutralized *and* a significant amount of its conjugate base, CH₃COO[−]. We recognize this as a buffer solution, so we can use the Henderson–Hasselbalch equation to find the pH.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{\text{mmol conjugate base}}{\text{mmol acid}} = \text{p}K_a + \log \frac{\text{mmol CH}_3\text{COO}^-}{\text{mmol CH}_3\text{COOH}} \\ &= 4.74 + \log \frac{30.0}{50.0} = 4.74 + \log(0.600) = 4.74 + (-0.222) \\ &= 4.52 \end{aligned}$$

You should now work Exercises 54b to 54f.

► We are given the amounts of *both* reactants, so we recognize this as a *limiting reactant* problem. Review Section 3-3.

► Recall that *M* is equal to moles per liter or millimoles per milliliter.

► We could also solve this problem using the *K_a* expression as we did in Example 19-5.

More Complex Buffer Solutions

Living systems depend on buffers for pH control; most of these are complex buffers that contain a mixture of various acids and bases. Buffers can be made from weak acids/bases and the salts of *other* weak acids/bases. For example, we could make an acidic buffer from acetic acid and sodium bicarbonate (NaHCO₃, a salt of the weak acid carbonic acid). Or, we could make a basic buffer from NH₃ and NH₂(CH₃)₂Br (the salt of the weak base dimethylamine, HN(CH₃)₂). But it is more difficult to calculate pH's or other concentration values from these mixed buffer systems. We have limited our discussion and detailed examples to buffers that contain a weak acid/base and the salt of that *same* acid/base.

19-4 Acid–Base Indicators

In Section 11-2, we described acid–base titrations and the use of indicators to tell us when to stop a titration. Detection of the end point in an acid–base titration is only one of the important uses of indicators.

An **indicator** is an organic dye; its color depends on the concentration of H₃O⁺ ions, or the pH, in the solution. By the color an indicator displays, it “indicates” the acidity or basicity of a solution. Figure 19-1 displays solutions that contain three common indicators in solutions over the pH range 3 to 11. Carefully study Figure 19-1 and its legend.

► Phenolphthalein was the active component of the laxative Ex-Lax.

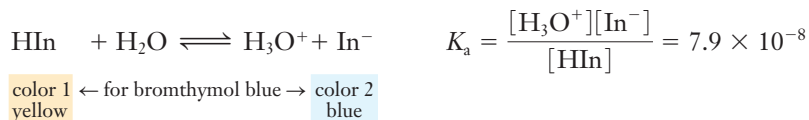
Unless otherwise noted, all content on this page is © Cengage Learning.



Bromthymol blue indicator is yellow in acidic solutions and blue in basic solutions.

The first indicators used were vegetable dyes. Litmus is a familiar example: red in acidic solution, blue in basic solution. Most of the indicators that we use in the laboratory today are synthetic compounds; that is, they have been made in laboratories by chemists. Phenolphthalein is the most common acid–base indicator. It is colorless in solutions of pH less than 8 ($[\text{H}_3\text{O}^+] > 10^{-8} \text{ M}$) and turns bright pink as pH approaches 10.

Many acid–base indicators are weak organic acids. An organic indicator acid can be symbolized by HIn , where “In” represents various complex organic groups. Bromthymol blue is such an indicator. Its acid ionization constant is 7.9×10^{-8} . We can represent its ionization in dilute aqueous solution and its ionization constant expression as



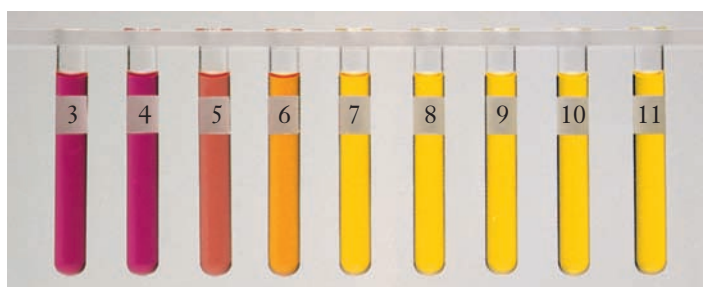
HIn represents nonionized acid molecules, and In^- represents the anion (conjugate base) of HIn. The essential characteristic of an acid–base indicator is that HIn and In^- must have quite different colors. The relative amounts of the two species determine the color of the solution. Adding an acid favors the reaction to the left and gives more HIn molecules (color 1). Adding a base favors the reaction to the right and gives more In^- ions (color 2). The ionization constant expression can be rearranged.

$$\frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = K_a \quad \text{so} \quad \frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_a}{[\text{H}_3\text{O}^+]}$$

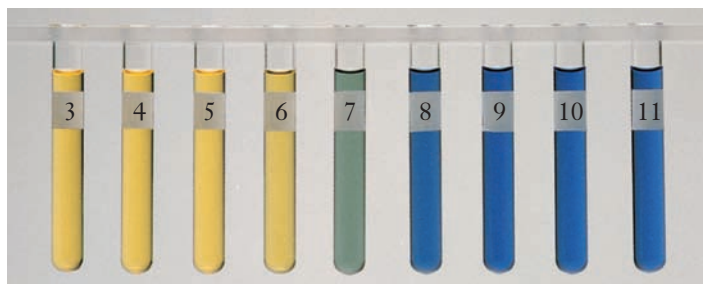
This shows clearly how the $[\text{In}^-]/[\text{HIn}]$ ratio depends on $[\text{H}_3\text{O}^+]$ (or on pH) and the K_a value for the indicator. As a rule of thumb, when $[\text{In}^-]/[\text{HIn}] \geq 10$, color 2 (the color of In^-) is observed; conversely, when $[\text{In}^-]/[\text{HIn}] \leq \frac{1}{10}$, color 1 (the color of HIn) is observed.

Universal indicators are mixtures of several acid–base indicators that display a continuous range of colors over a wide range of pH values. Figure 18-2 shows concentrated solu-

Figure 19-1 Three common indicators in solutions that cover the pH range 3 to 11 (the black numbers).



A Methyl red is red at pH 4 and below; it is yellow at pH 7 and above. Between pH 4 and pH 7 it changes from red to red-orange, to orange, to yellow.



B Bromthymol blue is yellow at pH 6 and below; it is blue at pH 8 and above. Between pH 6 and pH 8 it changes smoothly from yellow through green to blue.



C Phenolphthalein is colorless below pH 8 and bright pink above pH 10. It changes smoothly from colorless to bright pink in the pH range 8 to 10.

tions of a universal indicator in flat dishes so that the colors are very intense. The juice of red (purple) cabbage is a natural universal indicator (Figure 19-2).

One important use of universal indicators is in commercial indicator papers, which are small strips of paper impregnated with solutions of universal indicators. A strip of the paper is dipped into the solution of interest, and the color of the indicator on the paper indicates the pH of the solution. The photographs on page 717 illustrate the use of universal indicators to estimate pH. We shall describe the use of indicators in titrations more fully in Sections 19-5 and 19-6.

Titration Curves

19-5 Strong Acid/Strong Base Titration Curves

A **titration curve** is a plot of pH versus the amount (usually volume) of acid or base added. It displays graphically the change in pH as acid or base is added to a solution and shows how pH changes during the course of the titration.

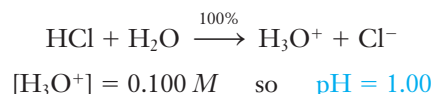
The **equivalence point** is the point at which chemically equivalent amounts of acid and base have reacted. The point at which the color of an indicator changes in a titration is known as the **end point**. It is determined by the K_a value for the indicator (see Section 19-4). Table 19-4 shows a few acid–base indicators and the pH ranges over which their colors change. Typically, color changes occur over a range of 1.5 to 2.0 pH units.

Ideally, the end point and the equivalence point in a titration should coincide.

In practice, we try to select an indicator whose range of color change includes the equivalence point. We use the same procedures in both standardization and analysis to minimize any error arising from a difference between end point and equivalence point.

Review Section 11-2 before you consider the titration of 100.0 mL of a 0.100 *M* solution of HCl with a 0.100 *M* solution of NaOH. As we know, NaOH and HCl react in a 1:1 ratio. We calculate the pH of the solution at several stages as NaOH is added.

- Before any NaOH is added to the 0.100 *M* HCl solution:



The pH depends only on the initial concentration of strong acid.

- After 20.0 mL of 0.100 *M* NaOH has been added:

	HCl	+	NaOH	→	NaCl	+ H ₂ O
start	10.0 mmol		2.0 mmol		0 mmol	
change	−2.0 mmol		−2.0 mmol		+2.0 mmol	
after rxn	8.0 mmol		0 mmol		2.0 mmol	

The concentration of unreacted HCl in the total volume of 120. mL is

$$M_{\text{HCl}} = \frac{8.00 \text{ mmol HCl}}{120. \text{ mL}} = 0.067 \text{ M HCl}$$

$$[\text{H}_3\text{O}^+] = 6.7 \times 10^{-2} \text{ M} \quad \text{so} \quad \text{pH} = 1.17$$

The pH depends on the amount of strong acid not yet neutralized.

- After 50.0 mL of 0.100 *M* NaOH has been added (midpoint of the titration):

	HCl	+	NaOH	→	NaCl	+ H ₂ O
start	10.0 mmol		5.0 mmol		0 mmol	
change	−5.0 mmol		−5.0 mmol		+5.0 mmol	
after rxn	5.0 mmol		0 mmol		5.0 mmol	



Anthocyanin pigments, which are found in many plants (see the geranium photo at the beginning of this chapter) are naturally occurring acid–base indicators. There are more than 400 organic molecules that belong to the anthocyanin family. Many red or purple foods, such as blueberries, raspberries, and grapes, contain anthocyanins. Some of these anthocyanins can also act as beneficial antioxidants in the diet. Antioxidants help to protect living cells against the damaging effects of free radicals and are thought to help inhibit the premalignant growth of some cancer cells.



Figure 19-2 The juice of the red (purple) cabbage is a naturally occurring universal indicator. From left to right are solutions of pH 1, 4, 7, 10, and 13.

- ▶ Titrations are typically done with 50-mL or smaller burets. We have used 100. mL of solution in this discussion to simplify the arithmetic.
- ▶ If one prefers, these calculations can be done using moles and liters in the place of millimoles and milliliters.

Table 19-4 Range and Color Changes of Some Common Acid–Base Indicators

Indicators	pH Scale												
	1	2	3	4	5	6	7	8	9	10	11	12	13
methyl orange	red			yellow									
methly red	red				yellow								
bromthymol blue	yellow						blue						
neutral red	red						yellow						
phenolphthalein	colorless								bright pink			colorless beyond 13.0	



Some household products. Each solution contains a few drops of a universal indicator. A color of yellow or red indicates a pH less than 7 (acidic). A green to purple color indicates a pH greater than 7 (basic).

► A strong base/strong acid salt does not undergo hydrolysis (Section 18–7).

$$M_{\text{HCl}} = \frac{5.00 \text{ mmol HCl}}{150. \text{ mL}} = 0.033 \text{ M HCl}$$

$$[\text{H}_3\text{O}^+] = 3.3 \times 10^{-2} \text{ M} \quad \text{so} \quad \text{pH} = 1.48$$

The pH depends on the amount of strong acid not yet neutralized.

4. After 100. mL of 0.100 M NaOH has been added:

	HCl	+	NaOH	→	NaCl	+	H ₂ O
start	10.0 mmol		10.0 mmol		0 mmol		
change	–10.0 mmol		–10.0 mmol		+10.0 mmol		
after rxn	0 mmol		0 mmol		10.0 mmol		

We have added enough NaOH to neutralize the HCl exactly, so *this is the equivalence point. A strong acid and a strong base react to give a neutral salt solution, so* $\text{pH} = 7.00$.

5. After 110.0 mL of 0.100 M NaOH has been added:

	HCl	+	NaOH	→	NaCl	+	H ₂ O
start	10.0 mmol		11.0 mmol		0 mmol		
change	–10.0 mmol		–10.0 mmol		+10.0 mmol		
after rxn	0 mmol		1.0 mmol		10.0 mmol		

The pH is determined by the excess NaOH.

$$M_{\text{NaOH}} = \frac{1.0 \text{ mmol NaOH}}{210. \text{ mL}} = 0.0048 \text{ M NaOH}$$

$$[\text{OH}^-] = 4.8 \times 10^{-3} \text{ M} \quad \text{so} \quad \text{pOH} = 2.32 \quad \text{and} \quad \text{pH} = 11.68$$

After the equivalence point, the pH depends only on the concentration of excess strong base.

Table 19-5 displays the data for the titration of 100.0 mL of 0.100 M HCl by 0.100 M NaOH solution. A few additional points have been included to show the shape of the curve better. These data are plotted in Figure 19-3a. This titration curve has a long “vertical section” over which the pH changes very rapidly with the addition of very small amounts of base. The pH changes very sharply from 3.60 (at 99.5 mL NaOH added) to 10.40 (at 100.5 mL of NaOH added) in the vicinity of the equivalence point (100.0 mL NaOH added). The midpoint of the vertical section ($\text{pH} = 7.00$) is the equivalence point.

For this kind of titration there are four distinct types of calculation, one for each of the four regions of the titration curves.

1. Before any strong base is added, the pH depends on the strong acid alone.
2. After some strong base has been added, but before the equivalence point, the remaining (excess) strong acid determines the pH.
3. At the equivalence point, the solution is neutral because it contains only a strong base/strong acid salt (no hydrolysis).
4. Beyond the equivalence point, excess strong base determines the pH.



Charles D. Winters

A Acidic solution just before the color change occurs; indicator is yellow.

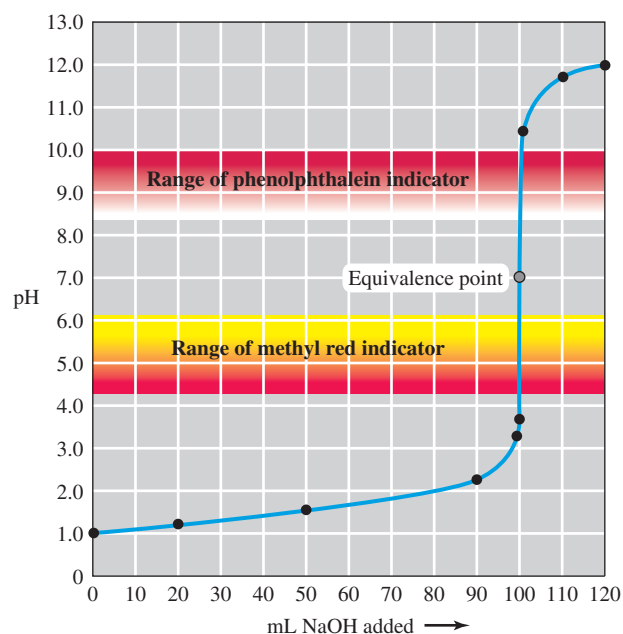


B Solution after several *small drops* of NaOH are added. The solution is now basic and the indicator is blue. The equivalence point occurs at pH = 7, which is the middle of the bromthymol blue indicator color change (Table 19-4). There is a very large change in pH (3.76 to 8.65 for this solution) right around the equivalence point for strong acid/strong base titrations.

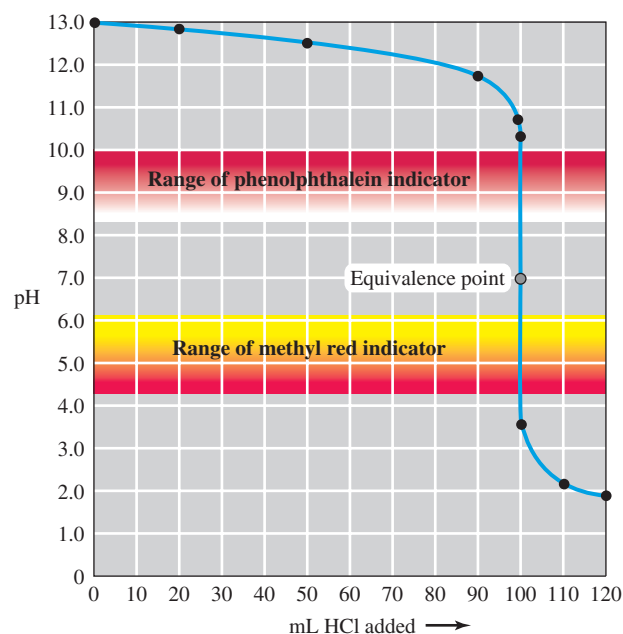
Titration of 0.100 M HCl with 0.100 M NaOH using bromthymol blue indicator.

Table 19-5 Titration Data for 100.0 mL of 0.100 M HCl Versus NaOH

mL of 0.100 M NaOH Added	mmol NaOH Added	mmol Excess Acid or Base	pH
0.0	0.00	10.0 H ₃ O ⁺	1.00
20.0	2.00	8.0	1.17
50.0	5.00	5.0	1.48
90.0	9.00	1.0	2.28
99.0	9.90	0.10	3.30
99.5	9.95	0.05	3.60
100.0	10.00	0.00 (eq. pt.)	7.00
100.5	10.05	0.05 OH ⁻	10.40
110.0	11.00	1.00	11.68
120.0	12.00	2.00	11.96



A The titration curve for 100. mL of 0.100 M HCl with 0.100 M NaOH. Note that the “vertical” section of the curve is quite long. The titration curves for other strong acids and bases are identical with this one *if* the same concentrations of acid and bases are used *and if* both are monoprotic.



B The titration curve for 100. mL of 0.100 M NaOH with 0.100 M HCl. This curve is similar to that in (a), but inverted.

Figure 19-3 Typical strong acid/strong base curves.

Unless otherwise noted, all content on this page is © Cengage Learning.

Ideally, the indicator color change should occur at $\text{pH} = 7.00$. For practical purposes, though, indicators with color changes in the pH range 4 to 10 can be used in the titration of strong acids and strong bases because the vertical portion of the titration curve is so long. Figure 19-3 shows the ranges of color changes for methyl red and phenolphthalein, two widely used indicators. Both fall within the vertical section of the NaOH/HCl titration curve, so either indicator would be suitable. When a strong acid is added to a solution of a strong base, the titration curve is inverted, but its essential characteristics are the same (see Figure 19-3b).

In Figure 19-3a, we see that the curve rises very slowly before the equivalence point. It then rises very rapidly near the equivalence point because there is no hydrolysis. The curve becomes almost flat beyond the equivalence point.

19-6 Weak Acid/Strong Base Titration Curves

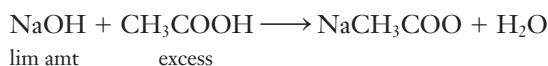
When a weak acid is titrated with a strong base, the curve is quite different in two important ways. (i) Once the addition of strong base begins, the solution is buffered *before* the equivalence point. (ii) The solution is basic *at* the equivalence point because a salt of a weak acid and a strong base undergoes hydrolysis (see Section 18-8) to give a basic solution.

As before, we can separate the calculations for this kind of titration into four distinct types, corresponding to four regions of the titration curves.

1. Before any base is added, the pH depends on the weak acid alone.
2. After some base has been added, but before the equivalence point, a series of weak acid/salt buffer solutions determines the pH .
3. At the equivalence point, hydrolysis of the anion of the weak acid determines the pH .
4. Beyond the equivalence point, excess strong base determines the pH .

Consider the titration of 100.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH solution. (The strong electrolyte is added to the weak electrolyte.)

1. Before any base is added, the pH is 2.89 (see Example 18-11 and Table 18-5).
2. As soon as some NaOH is added, but before the equivalence point, the solution is buffered because it contains both CH_3COOH and NaCH_3COO in significant concentrations.



For instance, after 20.0 mL of 0.100 M NaOH solution has been added, we have

	NaOH	$+ \text{CH}_3\text{COOH}$	$\longrightarrow$	$\text{NaCH}_3\text{COO} + \text{H}_2\text{O}$
start	2.00 mmol	10.00 mmol		0 mmol
change	-2.00 mmol	-2.00 mmol		$+2.00$ mmol
after rxn	0 mmol	8.00 mmol		2.00 mmol

We recognize that this is a buffer solution, so we can use the ratio (mmol conjugate base)/(mmol acid) in the Henderson–Hasselbalch equation as we did in Example 19-7.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{\text{mmol conjugate base}}{\text{mmol acid}} = \text{p}K_a + \log \frac{\text{mmol CH}_3\text{COO}^-}{\text{mmol CH}_3\text{COOH}} \\ &= 4.74 + \log \frac{2.00}{8.00} = 4.74 + \log(0.250) = 4.74 + (-0.602) = 4.14 \end{aligned}$$

After some NaOH has been added, the solution contains both NaCH_3COO and CH_3COOH , and so it is buffered until the equivalence point is reached. All points before the equivalence point are calculated in the same way.

► If it were not already known, we could calculate the pH of the weak acid solution in region 1 using the methods presented in Section 18-8.

STOP & THINK

The pH calculation in region 2 is that shown for partial neutralization in Example 19-7. Alternatively, we could use the K_a expression for these calculations as we did in Example 19-5.

3. At the equivalence point, the solution is 0.0500 *M* in NaCH₃COO.

	NaOH	+ CH ₃ COOH	→ NaCH ₃ COO + H ₂ O
start	10.0 mmol	10.0 mmol	0 mmol
change	-10.0 mmol	-10.0 mmol	+10.0 mmol
after rxn	0 mmol	0 mmol	10.0 mmol

$$M_{\text{NaCH}_3\text{COO}} = \frac{10.0 \text{ mmol NaCH}_3\text{COO}}{200. \text{ mL}} = 0.0500 \text{ M NaCH}_3\text{COO}$$

The pH of a 0.0500 *M* solution of NaCH₃COO is 8.72 (Example 18-20 shows a similar calculation). The solution is distinctly basic at the equivalence point because of the hydrolysis of the acetate ion.

4. Beyond the equivalence point, the concentration of the excess NaOH determines the pH of the solution just as it did in the titration of a strong acid.

Figure 19-4 shows the titration curve for 100.0 mL of 0.100 *M* CH₃COOH titrated with a 0.100 *M* solution of NaOH, and Table 19-6 lists several points on the titration curve. This titration curve has a short vertical section (pH ≈ 7 to 10), so many indicators would not be suitable. Phenolphthalein is the indicator commonly used to titrate weak acids with strong bases (see Table 19-4).

The titration curves for weak bases and strong acids are similar to those for weak acids and strong bases except that they are inverted (recall that strong is added to weak). Figure 19-5 displays the titration curve for 100.0 mL of 0.100 *M* aqueous ammonia titrated with 0.100 *M* HCl solution.

► Just *before* the equivalence point, the solution contains relatively high concentrations of NaCH₃COO and relatively low concentrations of CH₃COOH. Just *after* the equivalence point, the solution contains relatively high concentrations of NaCH₃COO and relatively low concentrations of NaOH, both basic components. In both regions our calculations are only approximations. Exact calculations of pH in these regions are too complicated to discuss here.

Table 19-6 Titration Data for 100.0 mL of 0.100 *M* CH₃COOH with 0.100 *M* NaOH

mL 0.100 <i>M</i> NaOH Added	mmol Base Added	mmol Excess Acid or Base	pH
0.0 mL	0	10.0 CH ₃ COOH	2.89
20.0 mL	2.00	8.00	4.14
50.0 mL	5.00	5.00	4.74
75.0 mL	7.50	2.50	5.22
90.0 mL	9.00	1.00	5.70
95.0 mL	9.50	0.50	6.02
99.0 mL	9.90	0.10	6.74
100.0 mL	10.0	0 (equivalence point)	8.72
101.0 mL	10.1	0.10 OH ⁻	10.70
110.0 mL	11.0	1.0	11.68
120.0 mL	12.0	2.0	11.96

19-7 Weak Acid/Weak Base Titration Curves

In titration curves for weak acids and weak bases, pH changes near the equivalence point are too gradual for color indicators to be used. The solution is buffered both before and after the equivalence point. Figure 19-6 shows the titration curve for 100.0 mL of 0.100 *M* CH₃COOH solution titrated with 0.100 *M* aqueous NH₃. The pH at the equivalence point might not be 7.0, depending on which weak base/weak acid salt is formed. The calculation of values along a weak acid/weak base titration curve (other than the initial pH and the equivalence point) is beyond the scope of this text.

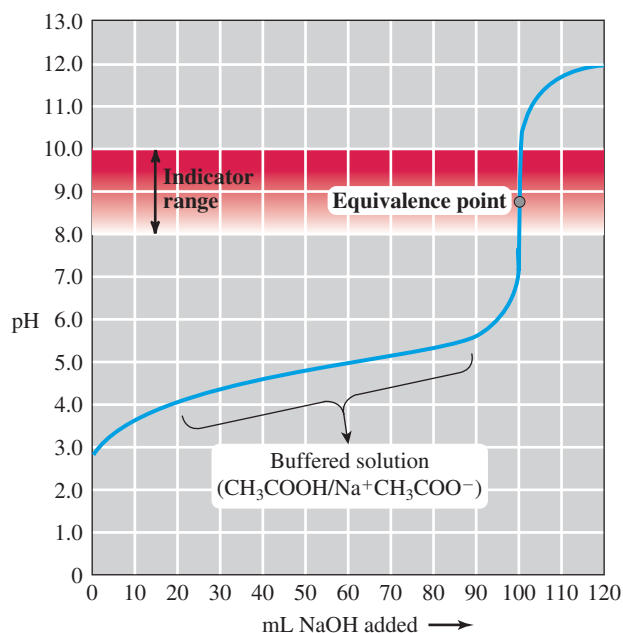


Figure 19-4 The titration curve for 100. mL of 0.100 M CH_3COOH with 0.100 M NaOH . The “vertical” section of this curve is much shorter than those in Figure 19-3 because the solution is buffered before the equivalence point. Methyl red indicator, which changes over the range 4.5 to 6.4, would obviously not be suitable for this titration.

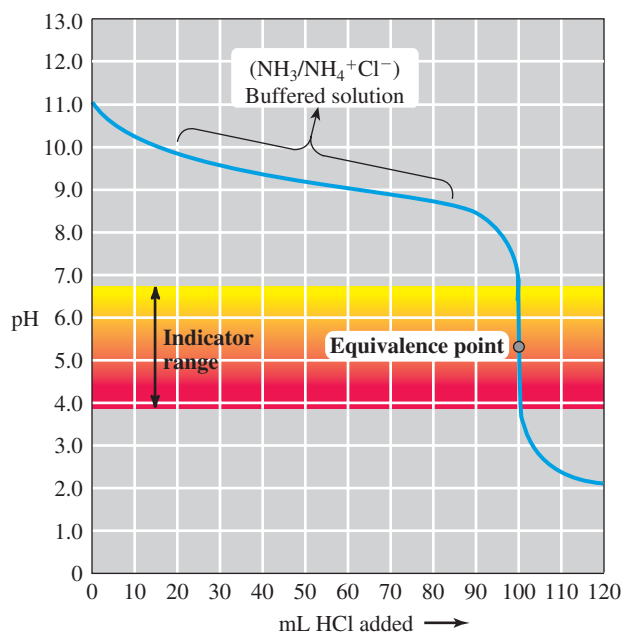


Figure 19-5 The titration curve for 100. mL of 0.100 M aqueous ammonia with 0.100 M HCl . The vertical section of the curve is relatively short because the solution is buffered before the equivalence point. The curve is very similar to that in Figure 19-4, but inverted. Phenolphthalein indicator, which changes over the range 8.0 to 10.0, should not be used for this titration.

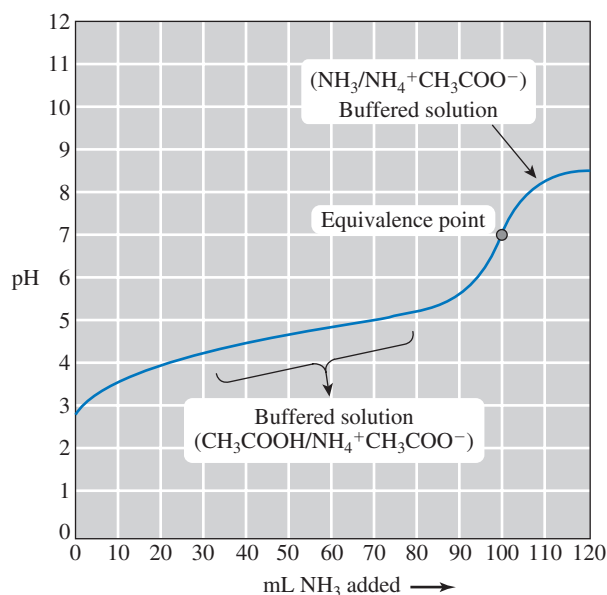


Figure 19-6 The titration curve for 100. mL of 0.100 M CH_3COOH with 0.100 M aqueous NH_3 . At the equivalence point for *this* weak acid/weak base titration, the pH is 7.0, but this is not true for all such combinations (see Section 18-10). Because the solution is buffered before and after the equivalence point, the pH changes very gradually near the equivalence point. Color indicators cannot be used in such titrations. Instead, physical methods such as conductivity measurements or pH electrode-based instruments can be used to detect the end point.



Problem-Solving Tip Titration Curves

You can consider a titration curve in four parts.

- 1. Initial solution** (before any titrant is added).
- 2. Region before the equivalence point.** This may or may not be buffered. The solution is buffered in this region if the substance being titrated is a weak acid or weak base. A 1:1 buffer is created *halfway* to the equivalence point. At this half-way point of a weak acid/strong base titration, the pK_a of the weak acid is equal to the observed pH. At the half-way point of a weak base/strong acid titration, the pK_b of the weak base is equal to the observed pOH (or $14 - \text{observed pH}$).
- 3. Equivalence point.** Its location depends on the concentrations of the acid and the base solutions; its pH depends on the strengths of the acid and base.
- 4. Region beyond the equivalence point.** This becomes nearly flat as more and more excess reactant is added. We often calculate only one or two points in this region.

Recognizing the four regions of a titration curve allows you to decide which kind of calculation is required.

19-8 Summary of Acid–Base Calculations

In this and the previous chapter, we have discussed several different types of acidic or basic solutions. Table 19-7 summarizes those many different types of solutions.

Table 19-7 A Review of the pH of Aqueous Solutions

Type of Aq. Solution	Example(s)	Resulting Chemistry or Type of Solution; Calculation	Section
<i>Strong acid</i> (represented as HX)	HNO ₃ or HCl	<i>Complete</i> ionization; reaction goes to completion to form H ₃ O ⁺ $\text{HX} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{X}^-$	18-1
<i>Strong base</i> [represented as MOH or M(OH) ₂]	NaOH or Ba(OH) ₂	<i>Complete</i> ionization; reaction goes to completion to form OH [−] $\text{MOH} \longrightarrow \text{M}^+ + \text{OH}^-$ $\text{M(OH)}_2 \longrightarrow \text{M}^{2+} + 2\text{OH}^-$	18-1
<i>Weak acid</i> (represented as HA)	CH ₃ COOH or HCN	<i>Partial</i> ionization; $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$ Must solve equilibrium expression involving K_a for the acid, using <i>equilibrium</i> concentrations: $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$	18-4
<i>Weak base</i> (represented as B)	NH ₃	<i>Partial</i> ionization; $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$ Must solve equilibrium expression involving K_b for the base, using <i>equilibrium</i> concentrations: $K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$	18-4
Salt of <i>strong base</i> & <i>strong acid</i> (represented as MX)	NaNO ₃ (salt of NaOH and HNO ₃)	No hydrolysis— <i>neutral solution</i>	18-7
Salt of <i>strong base</i> & <i>weak acid</i> (represented as MA)	NaCN (salt of NaOH and HCN)	<i>Hydrolysis</i> of conjugate base (A^-) of <i>weak acid</i> $\Rightarrow$ <i>basic solution</i> $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$ Solve weak base equilibrium for $\text{A}^- \text{ using } K_b \text{ for } \text{A}^- = \frac{K_w}{K_a \text{ for HA}}$	18-8

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 19-7 A Review of the pH of Aqueous Solutions—cont'd

Type of Aq. Solution	Example(s)	Resulting Chemistry or Type of Solution; Calculation	Section
Salt of <i>weak base</i> & <i>strong acid</i> (represented as BHX)	NH ₄ NO ₃ (salt of NH ₃ and HNO ₃)	<i>Hydrolysis</i> of conjugate acid (BH ⁺) of <i>weak base</i> ⇒ <i>acidic</i> solution $\text{BH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{B} + \text{H}_3\text{O}^+$ Solve weak acid equilibrium for BH ⁺ using $K_a \text{ for BH}^+ = \frac{K_w}{K_b \text{ for B}}$	18-9
Salt of <i>weak base</i> & <i>weak acid</i> (represented as BHA)	NH ₄ CN (salt of NH ₃ and HCN)	<i>Hydrolysis</i> of conjugate base (A ⁻) of <i>weak acid</i> ⇒ <i>basic</i> solution and <i>hydrolysis</i> of conjugate acid (BH ⁺) of <i>weak base</i> ⇒ <i>acidic</i> solution. This solution can be <i>basic</i> , <i>neutral</i> , or <i>acidic</i> , depending on which hydrolysis occurs to a greater extent; use K_b and K_a values for the <i>hydrolysis reactions</i> to tell which ion will be the dominant factor. (We did not do calculations for this type of salt.)	18-10
<i>Weak acid</i> & <i>salt</i> of its conjugate base (represented as HA & MA)	CH ₃ COOH + NaCH ₃ COO (or the product of the partial neutralization in a titration of a <i>weak acid</i> with a <i>strong base</i>)	Salt ionizes completely; $\text{MA} \longrightarrow \text{M}^+ + \text{A}^-$ Mixture of weak acid (HA) and its conjugate base (A ⁻) in significant concentrations gives a <i>buffer</i> . Use Henderson–Hasselbalch equation for acid/salt buffer (with ratio of initial concentrations, moles, or millimoles): $\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$	19-1, 19-2, 19-3
<i>Weak base</i> & <i>salt</i> of its conjugate acid (represented as B & BHX)	NH ₃ + NH ₄ Cl (or the product of the partial neutralization in a titration of a <i>weak base</i> with a <i>strong acid</i>)	Salt ionizes completely; $\text{NH}_4\text{Cl} \longrightarrow \text{NH}_4^+ + \text{Cl}^-$ Mixture of weak base (NH ₃) and its conjugate acid (NH ₄ ⁺) in significant concentrations gives a <i>buffer</i> . Use Henderson–Hasselbalch equation for base/salt buffer (with ratio of initial concentrations, moles, or millimoles): $\text{pOH} = \text{p}K_b + \log \frac{[\text{conjugate acid}]}{[\text{base}]}$	19-1, 19-2, 19-3

KEY TERMS

Buffer solution A solution that resists changes in pH when strong acids or strong bases are added. A buffer solution contains an acid and its conjugate base, so it can react with added base or acid. Common buffer solutions contain either (1) a weak acid and a soluble ionic salt of the weak acid, *or* (2) a weak base and a soluble ionic salt of the weak base.

Common ion effect Suppression of ionization of a weak electrolyte by the presence in the same solution of a strong electrolyte containing one of the same ions as the weak electrolyte.

End point The point at which an indicator changes color and a titration should be stopped.

Equivalence point The point at which chemically equivalent amounts of reactants have reacted.

Henderson–Hasselbalch equation An equation that enables us to calculate the pH or pOH of a buffer solution directly.

For acid/salt buffer
$$\text{pH} = \text{p}K_a + \log \frac{[\text{conj. base}]}{[\text{acid}]}$$

For base/salt buffer
$$\text{pOH} = \text{p}K_b + \log \frac{[\text{conj. acid}]}{[\text{base}]}$$

Can also be written in terms of ratio of moles or millimoles.

Indicator (for acid–base reactions) An organic compound that exhibits different colors in solutions of different acidities; used to indicate the point at which reaction between an acid and a base is complete.

Titration A procedure in which one solution is added to another solution until the chemical reaction between the two solutes is complete; usually the concentration of one solution is known and that of the other is unknown.

Titration curve (for acid–base titration) A plot of pH versus volume of acid or base solution added.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

All exercises in this chapter assume a temperature of 25°C unless they specify otherwise. Values of K_a and K_b can be found in Appendix F or will be specified in the exercise.

Basic Ideas

- (a) What is the relationship between pH, pOH, and pK_w ? (b) What is the relationship between K_a and pH? (c) What is the relationship between K_a and pOH?
- Define and give examples of (a) pK_a , (b) K_b , (c) pK_w , (d) pOH.
- Give the names and formulas of (a) five strong acids, (b) five weak acids, (c) four strong bases, (d) four weak bases.
- Write the balanced equation for an acid–base reaction that would produce each of the following salts; predict whether an aqueous solution of each salt is acidic, basic, or neutral. (a) NaNO_3 ; (b) Na_2S ; (c) $\text{Al}_2(\text{CO}_3)_3$; (d) $\text{Mg}(\text{CH}_3\text{COO})_2$; (e) $(\text{NH}_4)_2\text{SO}_4$.
- Write the balanced equation for an acid–base reaction that would produce each of the following salts; predict whether an aqueous solution of each salt is acidic, basic, or neutral. (a) CaF_2 ; (b) ZnSO_4 ; (c) CaCl_2 ; (d) K_3PO_4 ; (e) NH_4NO_3 .
- Under what circumstances can it be predicted that a neutral solution is produced by an acid–base reaction? (Hint: This question has more than one answer.)

The Common Ion Effect and Buffer Solutions

- Which of the following solutions are buffers? (Each solution was prepared by mixing and diluting appropriate quantities of the two solutes to yield the concentrations indicated.) Explain your decision for each solution. (a) 0.10 M HCN and 0.10 M NaCN; (b) 0.10 M NaCN and 0.10 M NaCl; (c) 0.10 M NH_3 and 0.10 M NH_4Br ; (d) 0.10 M NaOH and 0.90 M KOH.
- Which of the following solutions are buffers? (Each solution was prepared by mixing and diluting appropriate quantities of the two solutes to yield the concentrations indicated.) Explain your decision for each solution. (a) 1.0 M $\text{CH}_3\text{CH}_2\text{COOH}$ and 0.20 M $\text{NaCH}_3\text{CH}_2\text{COO}$; (b) 0.10 M NaOCl and 0.10 M HOCl; (c) 0.10 M NH_4Cl and 0.90 M NH_4Br ; (d) 0.10 M NaCl and 0.20 M HF.
- Which of these combinations would be the best to buffer the pH at approximately 9? (a) $\text{CH}_3\text{COOH}/\text{NaCH}_3\text{COO}$ (b) HCl/NaCl (c) $\text{NH}_3/\text{NH}_4\text{Cl}$

- Calculate pH for each of the following buffer solutions. (a) 0.15 M HF and 0.20 M KF; (b) 0.040 M CH_3COOH and 0.025 M $\text{Ba}(\text{CH}_3\text{COO})_2$.
- The pK_a of HOCl is 7.45. Calculate the pH of a solution that is 0.0222 M HOCl and 0.0444 M NaOCl.
- Calculate the concentration of OH^- and the pH for the following buffer solutions. (a) 0.25 M $\text{NH}_3(\text{aq})$ and 0.15 M NH_4NO_3 ; (b) 0.15 M $\text{NH}_3(\text{aq})$ and 0.20 M $(\text{NH}_4)_2\text{SO}_4$.
- Calculate the concentration of OH^- and the pH for the following solutions. (a) 0.45 M $\text{NH}_3(\text{aq})$ and 0.35 M NH_4NO_3 ; (b) 0.10 M aniline, $\text{C}_6\text{H}_5\text{NH}_2$, and 0.25 M anilinium chloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$.
- ▲ Buffer solutions are especially important in our body fluids and metabolism. Write net ionic equations to illustrate the buffering action of (a) the $\text{H}_2\text{CO}_3/\text{NaHCO}_3$ buffer system in blood and (b) the $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffer system inside cells.
- Calculate the ratio of $[\text{NH}_3]/[\text{NH}_4^+]$ concentrations that gives (a) solutions of pH = 9.55 and (b) solutions of pH = 9.10.
- We prepare two solutions as follows. In solution A 0.50 mole of potassium acetate is added to 0.25 mole of acetic acid and diluted to a final volume of 1.00 liter. In solution B 0.25 mole of potassium acetate is added to 0.50 mole of acetic acid and diluted to 1.00 liter. (a) Which solution is expected to have the lower pH? (b) Explain how you can reach your conclusion without calculating the pH of each solution.
- Compare the pH of a 0.30 M acetic acid solution to the pH of a solution composed of 0.30 M acetic acid to which 0.30 mole of sodium acetate per liter has been added.
- (a) Calculate $[\text{OH}^-]$ and $[\text{H}_3\text{O}^+]$ in a 0.30 M aqueous ammonia solution. The K_b for aqueous ammonia is 1.8×10^{-5} . (b) Calculate $[\text{OH}^-]$ and $[\text{H}_3\text{O}^+]$ of a buffer solution that is 0.30 M in NH_3 and 0.40 M in NH_4Cl .

Buffering Action

- Briefly describe why the pH of a given buffer solution remains nearly constant when small amounts of acid or base are added. Over what pH range would a given buffer exhibit the best buffering action (nearly constant pH)?
- Consider the ionization of formic acid, HCOOH.



What effect does the addition of sodium formate, NaHCOO, have on the fraction of formic acid molecules that undergo ionization in aqueous solution?

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

21. A solution is produced by dissolving 0.075 mole of formic acid and 0.065 mole of sodium formate in sufficient water to produce 1.00 L of solution. (a) Calculate the pH of this buffer solution. (b) Calculate the pH of the solution after an additional 0.020 mole of sodium formate is dissolved.
22. What is the pH of a solution that is 0.20 M in HClO_4 and 0.20 M KClO_4 ? Is this a buffer solution?
23. (a) Find the pH of a solution that is 0.50 M in formic acid and 0.30 M in sodium formate. (b) Find the pH after 0.050 mol HCl has been added to 1.00 liter of the solution.
24. One liter of 0.400 M NH_3 solution also contains 12.78 g of NH_4Cl . How much will the pH of this solution change if 0.142 mole of gaseous HCl is bubbled into it?
25. (a) Find the pH of a solution that is 0.11 M in nitrous acid and 0.15 M in sodium nitrite. (b) Find the pH after 0.14 mol of NaOH has been added to 1.00 liter of the solution.
26. (a) Find the pH of a solution that is 0.90 M in NH_3 and 0.80 M in NH_4Cl . (b) Find the pH of the solution after 0.10 mol of HCl has been added to 1.00 liter of the solution. (c) A solution was prepared by adding NaOH to pure water to give 1.00 liter of solution whose pH = 9.34. Find the pH of this solution after 0.10 mol of HCl has been added to it.
27. (a) Calculate the concentrations of CH_3COOH and CH_3COO^- in a solution in which their total concentration is 0.400 mol/L and the pH is 4.50. (b) If 0.100 mol of solid NaOH is added to 1.00 L of this solution, how much does the pH change?
28. ▲ A solution contains bromoacetic acid, BrCH_2COOH , and sodium bromoacetate, $\text{NaBrCH}_2\text{COO}$, with acid and salt concentrations that total 0.30 mol/L. If the pH is 3.50, what are the concentrations of the acid and the salt? $K_a = 2.0 \times 10^{-3}$ for BrCH_2COOH .
29. Calculate the concentration of propionate ion, $\text{CH}_3\text{CH}_2\text{COO}^-$, in equilibrium with 0.025 M $\text{CH}_3\text{CH}_2\text{COOH}$ (propionic acid) and 0.015 M H_3O^+ from hydrochloric acid. $K_a = 1.3 \times 10^{-5}$ for $\text{CH}_3\text{CH}_2\text{COOH}$.
30. Calculate the concentration of $\text{C}_2\text{H}_5\text{NH}_3^+$ in equilibrium with 0.012 M $\text{C}_2\text{H}_5\text{NH}_2$ (ethylamine) and 0.0040 M OH^- ion from sodium hydroxide. $K_b = 4.7 \times 10^{-4}$ for ethylamine.
31. ▲ Buffer capacity is defined as the number of moles of a strong acid or strong base that are required to change the pH of one liter of the buffer solution by one unit. What is the buffer capacity of a solution that is 0.10 M in acetic acid and 0.10 M in sodium acetate?
35. One liter of a buffer solution is prepared by dissolving 0.115 mol of NaNO_2 and 0.070 mol of HCl in water. What is the pH of this solution? If the solution is diluted twofold with water, what is the pH?
36. One liter of a buffer solution is made by mixing 500. mL of 1.25 M acetic acid and 500. mL of 0.300 M calcium acetate. What is the concentration of each of the following in the buffer solution? (a) CH_3COOH ; (b) Ca^{2+} ; (c) CH_3COO^- ; (d) H_3O^+ ; (e) What is the pH?
37. What must be the concentration of benzoate ion, $\text{C}_6\text{H}_5\text{COO}^-$, in a 0.0550 M benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, solution so that the pH is 5.10?
38. What must be the concentration of chloroacetic acid, CH_2ClCOOH , in a 0.015 M $\text{NaCH}_2\text{ClCOO}$ solution so that the pH is 2.75? $K_a = 1.4 \times 10^{-3}$ for CH_2ClCOOH .
39. What must be the concentration of NH_4^+ in a 0.075 M NH_3 solution so that the pH is 8.70?

Acid–Base Indicators

40. ● (a) What are acid–base indicators? (b) What are the essential characteristics of acid–base indicators? (c) What determines the color of an acid–base indicator in an aqueous solution?
41. K_a is 7.9×10^{-8} for bromthymol blue, an indicator that can be represented as HIn . HIn molecules are yellow, and In^- ions are blue. What color will bromthymol blue be in a solution in which (a) $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-4}$ M, and (b) pH = 10.30?
42. ▲ The indicator metacresol purple changes from yellow to purple at pH 8.2. At this point it exists in equal concentrations as the conjugate acid and the conjugate base. What are K_a and $\text{p}K_a$ for metacresol purple, a weak acid represented as HIn ?
43. ● A series of acid–base indicators can be used to estimate the pH of an unknown solution. The solution was colorless with phenolphthalein, yellow with methyl orange, and yellow with methyl red. Use the values given in Table 19-4 to determine the possible range of pH values of the solution.



Charles D. Winters

Preparation of Buffer Solutions

32. A buffer solution of pH = 5.10 is to be prepared from propionic acid and sodium propionate. The concentration of sodium propionate must be 0.60 mol/L. What should be the concentration of the acid? $K_a = 1.3 \times 10^{-5}$ for $\text{CH}_3\text{CH}_2\text{COOH}$.
33. We need a buffer with pH = 9.25. It can be prepared from NH_3 and NH_4Cl . What must be the $[\text{NH}_4^+]/[\text{NH}_3]$ ratio?
34. What volumes of 0.125 M acetic acid and 0.065 M NaOH solutions must be mixed to prepare 1.00 L of a buffer solution of pH = 4.50 at 25°C?

44. ● A series of acid–base indicators can be used to estimate the pH of an unknown solution. The solution was colorless in phenolphthalein, blue in bromthymol blue, and yellow in methyl orange. Use the values given in Table 19-4 to determine the possible range of pH values of the solution.

45. ● Use Table 19-4 to choose one or more indicators that could be used to “signal” reaching a pH of (a) 3.5; (b) 7.0; (c) 10.3; (d) 8.0.
46. A solution of 0.020 *M* acetic acid is to be titrated with a 0.025 *M* NaOH solution. What is the pH at the equivalence point? Choose an appropriate indicator for the titration.
47. Demonstrate mathematically that neutral red is red in solutions of pH 3.00, whereas it is yellow in solutions of pH 10.00. HIn is red, and In[−] is yellow. K_a is 2.0×10^{-7} .
51. A 36.30-mL sample of 0.245 *M* HNO₃ solution is titrated with 0.213 *M* KOH. Calculate the pH of the solution (a) before the addition of KOH and after the addition of (b) 6.15 mL, (c) 13.20 mL, (d) 26.95 mL, (e) 38.72 mL, (f) 42.68 mL of KOH solution.
52. A 22.0-mL sample of 0.145 *M* HCl solution is titrated with 0.106 *M* NaOH. Calculate the pH of the solution (a) before the addition of NaOH and after the addition of (b) 11.10 mL, (c) 24.0 mL, (d) 41.0 mL, (e) 54.4 mL, (f) 63.6 mL of NaOH solution.

Strong Acid/Strong Base Titration Curves

48. ▲ Make a rough sketch of the titration curve expected for the titration of a strong acid with a strong base. What determines the pH of the solution at the following points? (a) no base added; (b) half-equivalence point (the point at which one-half of the titrant volume required to reach the equivalence point has been added); (c) equivalence point; (d) excess base added. Compare your curve with Figure 19-3a.



Charles D. Winters

For Exercises 49, 54, 65, and 66, calculate and tabulate [H₃O⁺], [OH[−]], pH, and pOH at the indicated points as we did in Table 19-5. In each case assume that pure acid (or base) is added to exactly 1 L of a 0.0100 molar solution of the indicated base (or acid). This simplifies the arithmetic because we may assume that the volume of each solution is constant throughout the titration. Plot each titration curve with pH on the vertical axis and moles of base (or acid) added on the horizontal axis.

49. Solid NaOH is added to 1.00 L of 0.0500 *M* HCl solution. Number of moles of NaOH added: (a) none; (b) 0.00500; (c) 0.01500; (d) 0.02500 (50% titrated); (e) 0.03500; (f) 0.04500; (g) 0.04750; (h) 0.0500 (100% titrated); (i) 0.0525; (j) 0.0600; (k) 0.0750 (50% excess NaOH). List the indicators in Table 19-4 that could be used in this titration.
50. A 25.00-mL sample of 0.1500 *M* HNO₃ is titrated with 0.100 *M* NaOH. Calculate the pH of the solution (a) before the addition of NaOH and after the addition of (b) 6.00 mL, (c) 15.00 mL, (d) 30.00 mL, (e) 37.44 mL, (f) 45.00 mL of NaOH solution.
53. ● Make a rough sketch of the titration curve expected for the titration of a weak monoprotic acid with a strong base. What determines the pH of the solution at the following points? (a) no base added; (b) half-equivalence point (the point at which one-half of the titrant volume required to reach the equivalence point has been added); (c) equivalence point; (d) excess base added. Compare your curve to Figure 19-4.
54. (See instructions preceding Exercise 49.) Solid NaOH is added to exactly 1 L of 0.0200 *M* CH₃COOH solution. Number of moles NaOH added: (a) none; (b) 0.00400; (c) 0.00800; (d) 0.01000 (50% titrated); (e) 0.01400; (f) 0.01800; (g) 0.01900; (h) 0.0200 (100% titrated); (i) 0.0210; (j) 0.0240; (k) 0.0300 (50% excess NaOH). List the indicators in Table 19-4 that could be used in this titration.
55. A 44.0-mL sample of 0.202 *M* CH₃COOH solution is titrated with 0.185 *M* NaOH. Calculate the pH of the solution (a) before the addition of any NaOH solution and after the addition of (b) 15.5 mL, (c) 20.0 mL, (d) 24.0 mL, (e) 27.2 mL, (f) 48.0 mL, (g) 50.2 mL of NaOH solution.
56. A 32.44-mL sample of 0.182 *M* CH₃COOH solution is titrated with 0.185 *M* NaOH. Calculate the pH of the solution (a) before the addition of any NaOH solution and after the addition of (b) 15.55 mL, (c) 20.0 mL, (d) 24.02 mL, (e) 27.2 mL, (f) 31.91 mL, (g) 33.12 mL of NaOH solution.
57. A solution contains an unknown weak monoprotic acid, HA. It takes 46.24 mL of NaOH solution to titrate 50.00 mL of the HA solution to the equivalence point. To another 50.00-mL sample of the same HA solution, 23.12 mL of the same NaOH solution is added. The pH of the resulting solution in the second experiment is 5.14. What are K_a and pK_a of HA?
58. ▲ Calculate the pH at the equivalence point of the titration of 100.0 mL of each of the following with 0.1500 *M* KOH: (a) 1.200 *M* acetic acid; (b) 0.1200 *M* acetic acid; (c) 0.06000 *M* acetic acid.
59. Describe, quantitatively, how the concentration of hydronium ion, [H₃O⁺], is calculated in the titration of a weak acid with a strong base: (a) before any base is added, (b) after some base has been added, but before the equivalence point, (c) at the equivalence point, and (d) beyond the equivalence point.



Weak Base/Strong Acid Titration Curves

60. A 20.00-mL sample of 0.220 *M* triethylamine, $(\text{CH}_3\text{CH}_2)_3\text{N}$, is titrated with 0.544 *M* HCl.

$$K_b [(\text{CH}_3\text{CH}_2)_3\text{N}] = 5.2 \times 10^{-4}$$

- Write a balanced net ionic equation for the titration.
 - How many mL of HCl are required to reach the equivalence point?
 - Calculate $[(\text{CH}_3\text{CH}_2)_3\text{N}]$, $[(\text{CH}_3\text{CH}_2)_3\text{NH}^+]$, $[\text{H}^+]$, and $[\text{Cl}^-]$ at the equivalence point. (Assume that volumes are additive.)
 - What is the pH at the equivalence point?
61. What is the pH of the solution that results from adding 25.0 mL of 0.12 *M* HCl to 25.0 mL of 0.43 *M* NH_3 ?
62. Suppose a small amount of a strong acid is added to an aniline buffer system ($\text{C}_6\text{H}_5\text{NH}_2/\text{C}_6\text{H}_5\text{NH}_3^+$). What is the net ionic equation for the main reaction that occurs to largely neutralize the added acid?
63. If 1 *M* solutions of each of the following compounds were prepared, which one would have the highest pH?
(a) ammonium acetate ($\text{NH}_4\text{CH}_3\text{COO}$); (b) potassium chloride (KCl); (c) sodium cyanide (NaCN); (d) ammonium nitrate (NH_4NO_3); (e) hydrochloric acid (HCl).

Mixed Exercises

64. Give the name and formula of a compound that could be combined with each one of the following compounds to produce a buffer solution: HNO_2 , NaCN , $(\text{NH}_4)_2\text{SO}_4$, NH_3 , HCN , $(\text{CH}_3)_3\text{N}$.
65. ▲ (See instructions preceding Exercise 49.) Gaseous HCl is added to 1.00 L of 0.0100 *M* aqueous ammonia solution. Number of moles HCl added: (a) none; (b) 0.00100; (c) 0.00300; (d) 0.00500 (50% titrated); (e) 0.00700; (f) 0.00900; (g) 0.00950; (h) 0.0100 (100% titrated); (i) 0.0105; (j) 0.0120; (k) 0.0150 (50% excess HCl). List the indicators in Table 19-4, that could be used in this titration.
66. ▲ (See instructions preceding Exercise 49.) Gaseous NH_3 is added to 1.00 L of 0.0100 *M* HNO_3 solution. Number of moles NH_3 added: (a) none; (b) 0.00100; (c) 0.00400; (d) 0.00500 (50% titrated); (e) 0.00900; (f) 0.00950; (g) 0.0100 (100% titrated); (h) 0.0105; (i) 0.0130. What is the major difference between the titration curve for the reaction of HNO_3 and NH_3 and the other curves you have plotted? Consult Table 19-4. Can you suggest a satisfactory indicator for this titration?
67. Compare the pH of 0.54 *M* NaCl with the pH of 0.54 *M* NaOCl.
68. Compare the pH of 0.54 *M* NaCl with the pH of 0.54 *M* NH_4Cl .

Conceptual Exercises

69. Why do we need acid–base indicators that change at pH values other than 7?
70. The indicator indigo carmine changes from blue in acid to yellow in base. It is a weak acid with a K_a of 6×10^{-13} . At approximately what pH does indigo carmine change color?

71. In 100 mL of 0.100 *M* hypochlorous acid, HClO, the pH is 4.2, and the concentration of hypochlorite ion, ClO^- , is 6×10^{-5} . Describe what would happen if 100 mL of 0.100 *M* NaClO were added to it. (Include the effects, if any, on the pH and on the concentrations of HClO and ClO^- .)
72. The value of K_b for dimethylamine, $(\text{CH}_3)_2\text{NH}$, is 7.4×10^{-4} . Suppose dimethylammonium chloride, $(\text{CH}_3)_2\text{NH}_2\text{Cl}$, is dissolved in water. (a) Write the chemical equation for the dissociation of $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ in water. (b) Write the chemical equation for the hydrolysis reaction which then occurs. (c) Describe the resulting solution as acidic, basic, or neutral.
73. When methylamine, CH_3NH_2 , dissolves in water, it partially ionizes, producing the methylammonium ion, CH_3NH_3^+ :



$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

What effect, if any, would dissolving methylammonium chloride [$\text{CH}_3\text{NH}_3\text{Cl}$], a soluble salt, in this solution have on the equilibrium reaction?

74. Ammonium hypochlorite, NH_4ClO , is the salt of ammonia, NH_3 , and hypochlorous acid, HClO. (a) What is the K_a for ammonium ion? (b) What is the K_b for hypochlorite ion? (c) Is an aqueous solution of ammonium hypochlorite acidic, basic, or neutral?
75. ● The pH of an equal molar acetic acid/sodium acetate buffer is 4.74. Draw a molecular representation of a small portion of this buffer solution. (You may omit the water molecules.) Draw another molecular representation of the solution after a very small amount of NaOH has been added.
76. ● Suppose you were asked on a laboratory test to outline a procedure to prepare a buffer solution of pH 8.0 using hydrocyanic acid, HCN. You realize that a pH of 8.0 is basic, and you find that the K_a of hydrocyanic acid is 4.0×10^{-10} . What is your response?
77. ● The odor of cooked fish is due to the presence of amines. This odor is lessened by adding lemon juice, which contains citric acid. Why does this work?
78. ● The *end point* of a titration is not the same as the *equivalence point* of a titration. Differentiate between these two concepts.
79. One function of our blood is to carry CO_2 from our tissues to our lungs. It is critical that the pH of our blood remains at 7.4 ± 0.05 . Our blood is buffered to maintain that pH range, and the primary buffer system is composed of $\text{HCO}_3^-/\text{H}_2\text{CO}_3$. (a) Calculate the ratio of HCO_3^- to H_2CO_3 in blood if there were no other buffers present. (b) Determine whether in the presence of the $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ system alone, our blood would be more effective as a buffer against the addition of acidic or basic solutions.

Building Your Knowledge

80. A 0.738-g sample of an unknown mixture composed only of NaCl and KHSO_4 required 36.8 mL of 0.115 *M* NaOH

for titration. What is the percent by mass of KHSO_4 in the mixture?

81. Acetylsalicylic acid, the active ingredient in aspirin, has a K_a value of 3.0×10^{-4} . We dissolve 0.0100 mole of acetylsalicylic acid in sufficient water to make 1.00 L of solution and then titrate it with 0.500 M NaOH solution. What is the pH at each of these points in the titration (a) before any of the NaOH solution is added, (b) at the equivalence point, (c) when a volume of NaOH solution has been added that is equal to half the amount required to reach the equivalence point?



82. ▲ What is the pH of a solution that is a mixture of HOCl and HOI, each at 0.30 M concentration?
83. An unknown amount of water is mixed with 350. mL of a 6.0 M NaOH solution. A 75.0-mL sample of the resulting solution is titrated to neutrality with 52.5 mL of 6.00 M HCl. (a) Calculate the concentration of the diluted NaOH solution. (b) What was the concentration of the NaOH solution before it was diluted? (c) What volume of water was added? Assume that the volumes were additive.
84. A 3.5-L container of HCl had no concentration noted on its label. A 20.00-mL sample of this unknown HCl solution is titrated to a pH of 7.0 by 34.0 mL of 3.00 M NaOH solution. Determine the volume of this HCl solution required to prepare 1.5 L of 0.75 M HCl solution.
85. Calculate the pH at the equivalence point for the titration of a solution containing 150.0 mg of ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$, with 0.1000 M HCl solution. The volume of the solution at the equivalence point is 250. mL. Select a suitable indicator. K_b for ethylamine appears in Exercise 30.

88. Use a web search engine to find lists of acid–base indicators. (a) Select an indicator that is not mentioned in this chapter and give its color and pH at each end of its transition range. (b) Determine what is meant by the statement “Vanilla extract has been described as an olfactory (acid–base) indicator.”
89. ●● Locate a table of acid–base indicators on the web. What color will each solution be at the indicated pH when a small amount of the specified indicator is also present? (a) pH 3, congo red; (b) pH 5, congo red; (c) pH 6, methyl orange; (d) pH 9, thymolphthalein.
90. The flowers shown below are hydrangeas, which function as natural pH indicators. Use an internet search engine such as <http://www.google.com> to locate information about the relationship between hydrangea color and soil acidity. What metal (in ionic form) is responsible for the color difference? What chemicals are commonly used by gardeners to lower and raise soil pH?



Hydrangeas

Beyond the Textbook

NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.*

86. Search the web for buffered aspirin for pets. (a) For which animals did you find a buffered aspirin product being commercially marketed? (b) Which company(ies) markets a buffered roast-beef-flavored aspirin (VETRIN)? What is the dosage of aspirin in each VETRIN tablet? (c) What other dosages can you find?
87. Use a web search engine to find common misconceptions or mistakes involving buffers. What common errors do you find?



Molecular Reasoning exercises



More Challenging exercises

Blue-Numbered

exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

Ionic Equilibria III: The Solubility Product Principle

20



The formation of caves and objects such as stalactites (“tight to ceiling”) and stalagmites (“mites are on the ground”) are based on acid–base and precipitation equilibria. CO_2 gas reacts with water to form carbonic acid (H_2CO_3), which is acidic enough to attack and dissolve limestone (calcium carbonate, CaCO_3), often the first stage of cave formation. Once a cave cavity is formed, the mineral solution dripping down from above can begin to precipitate the dissolved minerals (mainly calcium carbonate) to form the various features we see in caves.

Jeff Schultes/Shutterstock.com

OUTLINE

- 20-1** Solubility Product Constants
- 20-2** Determination of Solubility Product Constants
- 20-3** Uses of Solubility Product Constants
- 20-4** Fractional Precipitation; $Q_{\text{sp}} \geq K_{\text{sp}}$
- 20-5** Simultaneous Equilibria Involving Slightly Soluble Compounds
- 20-6** Dissolving Precipitates; $Q_{\text{sp}} < K_{\text{sp}}$

OBJECTIVES

After you have studied this chapter, you should be able to

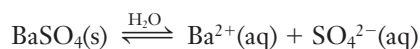
- ▶ Write solubility product constant expressions
- ▶ Explain how K_{sp} values are determined
- ▶ Use K_{sp} values in chemical calculations
- ▶ Recognize some common, slightly soluble compounds
- ▶ Describe fractional precipitation and how it can be used to separate ions
- ▶ Explain how simultaneous equilibria can be used to control solubility
- ▶ Describe some methods for dissolving precipitates

So far we have discussed mainly compounds that are quite soluble in water. Although most compounds dissolve in water to some extent, many are so slightly soluble that they are called “insoluble compounds.” We shall now consider those that are only very slightly soluble. As a rule of thumb, compounds that dissolve in water to the extent of 0.020 mole/liter or more are classified as soluble. Refer to the solubility guidelines (see Table 6-4) as necessary.

Slightly soluble compounds are important in many natural phenomena. Our bones and teeth are mostly calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, a slightly soluble compound. Many natural deposits of $\text{Ca}_3(\text{PO}_4)_2$ rock are mined and converted into agricultural fertilizer. Limestone caves have been formed by acidic water slowly dissolving away calcium carbonate, CaCO_3 . Sinkholes are created when acidic water dissolves away most of the underlying CaCO_3 . The remaining limestone can no longer support the weight above it, so it collapses, and a sinkhole is formed.

20-1 Solubility Product Constants

Suppose we add one gram of solid barium sulfate, BaSO_4 , to 1.0 liter of water at 25°C and stir until the solution is *saturated*. Very little BaSO_4 dissolves; most of the BaSO_4 remains as undissolved solid. Careful measurements of conductivity show that one liter of a saturated solution of barium sulfate contains only 0.0025 gram of dissolved BaSO_4 , no matter how much more solid BaSO_4 is added. The BaSO_4 that does dissolve is completely dissociated into its constituent ions.

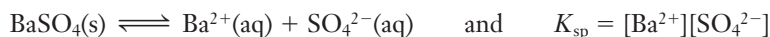


(We usually omit H_2O over the arrows in such equations; the (aq) phase of the ions tells us that we are dealing with aqueous solution.)

In equilibria that involve slightly soluble compounds in water, the equilibrium constant is called the **solubility product constant**, K_{sp} . The activity of the pure solid BaSO_4 is one (see Section 17-11).

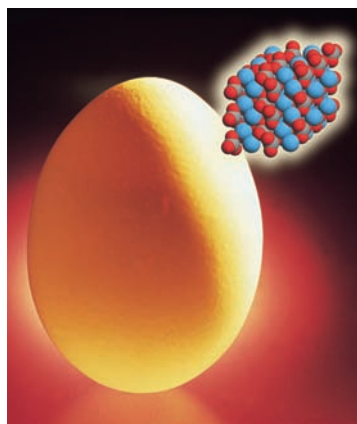
The concentration of the solid is never included in the equilibrium constant expression.

For a saturated solution of BaSO_4 in contact with solid BaSO_4 , we write



The solubility product constant for BaSO_4 is the product of the concentrations of its constituent ions in a saturated solution.

The *solubility product expression* for a compound is the product of the concentrations of its constituent ions, each raised to the power that corresponds to the number of ions in one formula unit of the compound. This product is constant at constant temperature for a saturated solution of the compound. This statement is the **solubility product principle**.



The calcium carbonate, CaCO_3 , in an eggshell has the same crystal structure as in the mineral calcite.



Charles Steele

The dissolution process of ions going into solution. During precipitation, ions are producing more solid as the ions leave the solution. For a saturated solution, the dissolution and precipitation rates are equal. For the very slightly soluble salts discussed in this chapter, the ion concentrations are very low compared with the concentration in this illustration.

The existence of a substance in the solid state can be indicated several ways. For example, $\text{BaSO}_4(\text{s})$, $\text{BaSO}_4\downarrow$, and $\text{BaSO}_4\downarrow$ are sometimes used to represent solid BaSO_4 . In this text we use the (s) notation for formulas of solid substances in equilibrium with their saturated aqueous solutions.

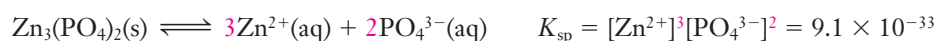
Consider dissolving slightly soluble calcium fluoride, CaF_2 , in H_2O .



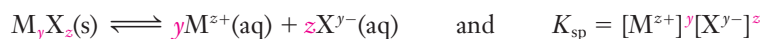
We often shorten the term “solubility product constant” to “solubility product.” Thus, the solubility products for barium sulfate, BaSO_4 , and for calcium fluoride, CaF_2 , are written as

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10} \quad K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^{-}]^2 = 3.9 \times 10^{-11}$$

The very small amount of solid zinc phosphate, $\text{Zn}_3(\text{PO}_4)_2$, that dissolves in water gives three zinc ions and two phosphate ions per formula unit.



Generally, we may represent the dissolution of a slightly soluble compound M_yX_z and its K_{sp} expression as



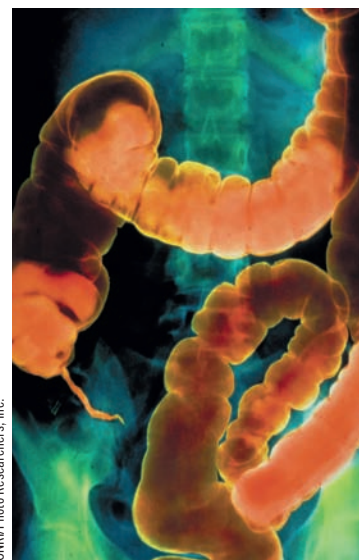
Charles D. Winters

A Barium sulfate, BaSO_4 , occurs in the mineral barite and has a relatively high density of 4.5 g/cm^3 .



B Calcium fluoride, CaF_2 , occurs in the mineral fluorite. The purple color is caused by defects in the crystal structure.

These two compounds are listed as “insoluble” in the solubility guidelines presented in Section 6-4. As we saw above, they are actually *very slightly soluble*.



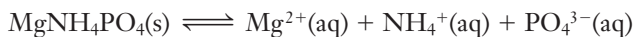
CNR/Photo Researchers, Inc.

An X-ray photo of the gastrointestinal tract. Barium sulfate is the “insoluble” substance taken orally before stomach X-rays are made because the barium atoms absorb X-rays well. Even though barium ions are quite toxic, barium sulfate can still be taken orally without danger. The compound is so insoluble that it passes through the digestive system essentially unchanged.

STOP & THINK

Remember to raise the concentration of each aqueous ion in the K_{sp} expression to the power of its coefficient in the balanced chemical equation.

In some cases, a compound contains more than two kinds of ions. Dissolution of the slightly soluble compound magnesium ammonium phosphate, MgNH_4PO_4 , in water and its solubility product expression are represented as



$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{NH}_4^+][\text{PO}_4^{3-}] = 2.5 \times 10^{-12}$$

Another way to express the solubility of a compound is **molar solubility**. This is defined as the number of moles that dissolve to give one liter of saturated solution.



Problem-Solving Tip You Must Recognize the Names and Formulas of Ions



To write the required equations for the dissolution and dissociation of salts, you must recognize the names and formulas of common, stable ions that are often present. Table 2-2 contains the names and formulas of several ions; since then you have learned others. Review these names and formulas carefully, and remember that formulas of ions must include their charges. Many of the ions you need to know are present in the salts listed in Appendix H.

► Unless otherwise indicated, solubility product constants and solubility data are given for 25°C (Appendix H).

► We frequently use statements such as “The solution contains 0.0025 gram of BaSO_4 .” What we mean is that 0.0025 gram of solid BaSO_4 *dissolves* to give a solution that contains equal concentrations of Ba^{2+} and SO_4^{2-} ions.

► 1.1×10^{-5} mole of solid BaSO_4 dissolves to give a liter of saturated solution.

► Calculated values may differ slightly from those found in tables due to data or rounding differences.

20-2 Determination of Solubility Product Constants

If the solubility of a compound is known, the molar solubility and the value of its solubility product can be calculated.

EXAMPLE 20-1 Molar Solubility and Product Constants

One (1.0) liter of saturated barium sulfate solution contains 0.0025 gram of dissolved BaSO_4 .

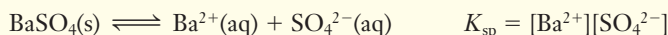
(a) What is the molar solubility of BaSO_4 ? (b) Calculate the solubility product constant for BaSO_4 .

Plan

(a) We write the equation for the dissolution of BaSO_4 and the expression for its solubility product constant, K_{sp} . From the solubility of BaSO_4 in H_2O , we calculate its molar solubility and the concentrations of the ions. (b) This lets us calculate K_{sp} .

Solution

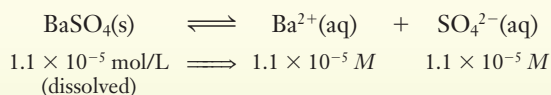
(a) In saturated solutions, solid and dissolved solute are in equilibrium. The equations for the dissolution of barium sulfate in water and its solubility product expression are



From the given solubility of BaSO_4 in H_2O , we can calculate its *molar solubility*.

$$\frac{? \text{ mol BaSO}_4}{\text{L}} = \frac{2.5 \times 10^{-3} \text{ g BaSO}_4}{1.0 \text{ L}} \times \frac{1 \text{ mol BaSO}_4}{233 \text{ g BaSO}_4} = 1.1 \times 10^{-5} \text{ mol BaSO}_4/\text{L} \quad (\text{dissolved})$$

(b) We know the molar solubility of BaSO_4 . The dissolution equation shows that each formula unit of BaSO_4 that dissolves produces one Ba^{2+} ion and one SO_4^{2-} ion.



In a saturated solution $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = 1.1 \times 10^{-5} \text{ M}$. Substituting these values into the K_{sp} expression for BaSO_4 gives the calculated value of K_{sp} .

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (1.1 \times 10^{-5})(1.1 \times 10^{-5}) = 1.2 \times 10^{-10}$$

You should now work Exercise 6.

EXAMPLE 20-2 Molar Solubility and Solubility Product Constant

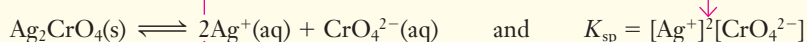
One (1.00) liter of a saturated solution of silver chromate at 25°C contains 0.0435 gram of dissolved Ag_2CrO_4 . Calculate (a) its molar solubility and (b) its solubility product constant.

Plan

We proceed as in Example 20-1.

Solution

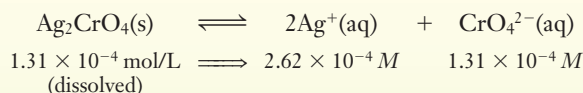
- (a) The equation for the dissolution of silver chromate in water and its solubility product expression are



The molar solubility of silver chromate is calculated first.

$$\frac{? \text{ mol Ag}_2\text{CrO}_4}{\text{L}} = \frac{0.0435 \text{ g Ag}_2\text{CrO}_4}{1.00 \text{ L}} \times \frac{1 \text{ mol Ag}_2\text{CrO}_4}{332 \text{ g Ag}_2\text{CrO}_4} = 1.31 \times 10^{-4} \text{ mol/L (dissolved)}$$

- (b) The equation for dissolution of Ag_2CrO_4 and its molar solubility give the concentrations of Ag^+ and CrO_4^{2-} ions in the saturated solution.



Substitution into the K_{sp} expression for Ag_2CrO_4 gives the value of K_{sp} .

$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (2.62 \times 10^{-4})^2(1.31 \times 10^{-4}) = 8.99 \times 10^{-12}$$

The calculated K_{sp} of Ag_2CrO_4 is 8.99×10^{-12} .

You should now work Exercise 8.

► 1.31×10^{-4} mole of solid Ag_2CrO_4 dissolves to give a liter of saturated solution.

STOP & THINK

Remember to raise $[\text{Ag}^+]$ to the power of its coefficient in the balanced chemical equation.

The molar solubility and K_{sp} values for BaSO_4 and Ag_2CrO_4 are compared in Table 20-1. These data show that the molar solubility of Ag_2CrO_4 is greater than that of BaSO_4 . The K_{sp} for Ag_2CrO_4 , however, is less than the K_{sp} for BaSO_4 because the expression for Ag_2CrO_4 contains a *squared* term, $[\text{Ag}^+]^2$.

Table 20-1 Comparison of Solubilities of BaSO_4 and Ag_2CrO_4

Compound	Molar Solubility	K_{sp}
BaSO_4	$1.1 \times 10^{-5} \text{ mol/L}$	$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$
Ag_2CrO_4	$1.3 \times 10^{-4} \text{ mol/L}$	$[\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 9.0 \times 10^{-12}$

STOP & THINK

Values of solubility product constants are usually tabulated to only two significant figures. Note that although the Ag_2CrO_4 is more soluble (higher molar solubility), it has a smaller K_{sp} value relative to BaSO_4 . One can only directly compare K_{sp} values for compounds with the same ion ratio.

If we compare K_{sp} values for two 1:1 compounds, for example, AgCl and BaSO_4 , the compound with the larger K_{sp} value has the higher molar solubility. The same is true for any two compounds that have the same ion ratio, for example, the 1:2 compounds CaF_2 and $\text{Mg}(\text{OH})_2$ and the 2:1 compound Ag_2CO_3 .

$$\begin{aligned} K_{\text{sp}}(\text{AgCl}) &= 1.8 \times 10^{-10} \\ K_{\text{sp}}(\text{BaSO}_4) &= 1.1 \times 10^{-10} \end{aligned}$$

The molar solubility of AgCl is only slightly greater than that of BaSO_4 .

If two compounds have the *same ion ratio*, the one with the larger K_{sp} will have the greater *molar* solubility.

Appendix H lists some K_{sp} values. Refer to it as needed.



Problem-Solving Tip It's Important to Know the Difference Between Solubility, Molar Solubility, and Solubility Product Expression

Often you need to know which of the following is given or which is asked for. Be sure you have a clear understanding of their definitions.

- ▶ The *solubility* of a compound is the amount of the compound that dissolves in a specified volume of solution. Solubility is usually expressed as either grams per liter or grams per 100 mL.
- ▶ The *molar solubility* of a compound is the number of moles of the compound that dissolve to give one liter of saturated solution. It is expressed in moles per liter.
- ▶ The *solubility product expression* for a compound is the product of the molar concentrations of its constituent ions, each raised to the power that corresponds to the number of ions in one formula unit of the compound. Like all equilibrium constants, it has no dimensions.

20-3 Uses of Solubility Product Constants

When the solubility product for a compound is known, the solubility of the compound in H_2O can be calculated, as the following example illustrates.

EXAMPLE 20-3 Molar Solubilities from K_{sp} Values

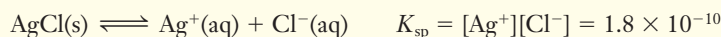
Calculate the molar solubilities, concentrations of the constituent ions, and solubilities in grams per liter for (a) silver chloride, AgCl ($K_{\text{sp}} = 1.8 \times 10^{-10}$), and (b) zinc hydroxide, $\text{Zn}(\text{OH})_2$ ($K_{\text{sp}} = 4.5 \times 10^{-17}$).

Plan

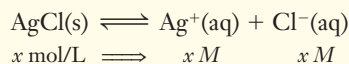
We are given the value for each solubility product constant. In each case we write the appropriate balanced equation, represent the equilibrium concentrations, and then substitute into the K_{sp} expression.

Solution

- (a) The equation for the dissolution of silver chloride and its solubility product expression are



Each formula unit of AgCl that dissolves produces one Ag^+ and one Cl^- . We let $x = \text{mol/L}$ of AgCl that dissolves, that is, the molar solubility.



Substitution into the solubility product expression gives

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (x)(x) = 1.8 \times 10^{-10} \quad x^2 = 1.8 \times 10^{-10} \quad x = 1.3 \times 10^{-5}$$

$x = \text{molar solubility of AgCl} = 1.3 \times 10^{-5} \text{ mol/L}$

One liter of saturated AgCl contains 1.3×10^{-5} mole of dissolved AgCl at 25°C . From the balanced equation, we know the concentrations of the constituent ions.

$$x = \text{molar solubility} = [\text{Ag}^+] = [\text{Cl}^-] = 1.3 \times 10^{-5} \text{ mol/L} = 1.3 \times 10^{-5} M$$

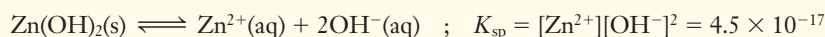
Now we can calculate the mass of dissolved AgCl in one liter of saturated solution.

$$\frac{? \text{ g AgCl}}{\text{L}} = \frac{1.3 \times 10^{-5} \text{ mol AgCl}}{\text{L}} \times \frac{143 \text{ g AgCl}}{1 \text{ mol AgCl}} = 1.9 \times 10^{-3} \text{ g AgCl/L}$$

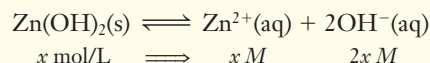
A liter of saturated AgCl solution contains only 0.0019 g of dissolved AgCl .

▶ The values of K_{sp} are obtained from Appendix H.

- (b) The equation for the dissolution of zinc hydroxide, Zn(OH)_2 , in water and its solubility product expression are



We let x = molar solubility, so $[\text{Zn}^{2+}] = x$ and $[\text{OH}^{-}] = 2x$, and we have



Substitution into the solubility product expression gives

$$[\text{Zn}^{2+}][\text{OH}^{-}]^2 = (x)(2x)^2 = 4.5 \times 10^{-17}$$

$$4x^3 = 4.5 \times 10^{-17} \quad ; \quad x^3 = 11 \times 10^{-18} \quad ; \quad x = 2.2 \times 10^{-6}$$

$$x = \text{molar solubility of Zn(OH)}_2 = 2.2 \times 10^{-6} \text{ mol Zn(OH)}_2/\text{L}$$

$$[\text{Zn}^{2+}] = x = 2.2 \times 10^{-6} M \quad \text{and} \quad [\text{OH}^{-}] = 2x = 4.4 \times 10^{-6} M$$

We can now calculate the mass of dissolved Zn(OH)_2 in one liter of saturated solution.

$$\frac{? \text{ g Zn(OH)}_2}{\text{L}} = \frac{2.2 \times 10^{-6} \text{ mol Zn(OH)}_2}{\text{L}} \times \frac{99 \text{ g Zn(OH)}_2}{1 \text{ mol Zn(OH)}_2} = 2.2 \times 10^{-4} \text{ g Zn(OH)}_2/\text{L}$$

A liter of saturated Zn(OH)_2 solution contains only 0.00022 g of dissolved Zn(OH)_2 .

You should now work Exercise 16.

STOP & THINK

The $[\text{OH}^{-}]$ is twice the molar solubility of Zn(OH)_2 because each formula unit of Zn(OH)_2 produces two OH^{-} ions.



Problem-Solving Tip The Dissolution of a Slightly Soluble Base Is Not a K_b Problem

The K_{sp} expression describes the equilibrium between a slightly soluble compound and its ions; in Example 20-3(b) one of those ions is OH^{-} . A K_b expression describes the equilibrium between a *soluble* basic species, for example, the ammonia molecule or the acetate ion, and the products it forms in solution, including OH^{-} . Do you see why the dissolution of Zn(OH)_2 is not a K_b problem? But even though it is not formally a K_b problem, we can still determine the solution's pH (or pOH). We found that $[\text{OH}^{-}] = 4.4 \times 10^{-6} M$ in a *saturated* Zn(OH)_2 solution. From this we can calculate that $\text{pOH} = 5.36$ and $\text{pH} = 8.64$. A saturated Zn(OH)_2 solution is not very basic because Zn(OH)_2 is not very soluble in H_2O . The $[\text{OH}^{-}]$ is only about 44 times greater than it is in pure water.

The Common Ion Effect in Solubility Calculations

Recall from Section 19-1 that the common ion effect is a special case of LeChatelier's Principle. Thus, the common ion effect applies to solubility equilibria just as it does to other ionic equilibria. Silver acetate, AgCH_3COO , is a slightly soluble salt:



If we add another salt that provides one of the product ions, say Ag^{+} (from AgNO_3), this dissolution reaction is shifted to the *left* (LeChatelier's Principle). Example 20-4 illustrates this effect.

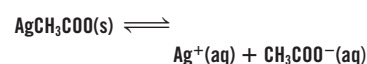
EXAMPLE 20-4 Molar Solubilities and the Common Ion Effect

For magnesium fluoride, MgF_2 , $K_{\text{sp}} = 6.4 \times 10^{-9}$. (a) Calculate the molar solubility of magnesium fluoride in pure water. (b) Calculate the molar solubility of MgF_2 in 0.10 M sodium fluoride, NaF , solution. (c) Compare these molar solubilities.



Charles D. Winters

The tube at the left contains a saturated solution of silver acetate, AgCH_3COO . When 1 M AgNO_3 is added to the tube, the equilibrium



shifts to the left and additional AgCH_3COO precipitates. This demonstrates the common ion effect.

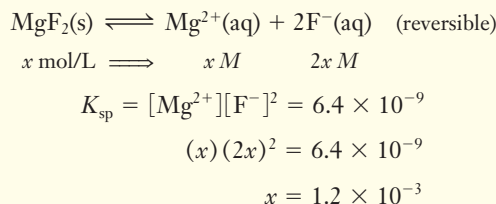
Unless otherwise noted, all content on this page is © Cengage Learning.

Plan

For part (a), we write the appropriate chemical equations and solubility product expression, designate the equilibrium concentrations, and then substitute into the solubility product expression. For part (b), we recognize that NaF is a soluble ionic compound that is completely dissociated into its ions. MgF_2 is a slightly soluble compound. Both compounds produce F^- ions, so this is a common ion effect problem. We write the appropriate chemical equations and solubility product expression, represent the equilibrium concentrations, and substitute into the solubility product expression. For part (c), we compare the molar solubilities by calculating their ratio.

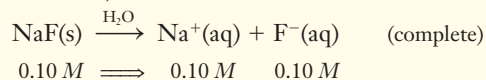
Solution

- (a) We let x = molar solubility for MgF_2 , a slightly soluble salt.

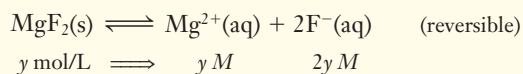


molar solubility of MgF_2 in pure water = $1.2 \times 10^{-3} \text{ M}$

- (b) NaF is a soluble ionic salt, so 0.10 M NaF contains 0.10 M F^- :



We let y = molar solubility for MgF_2 , a slightly soluble salt.



The total $[\text{F}^-]$ is 0.10 M from NaF *plus* $2y \text{ M}$ from MgF_2 , or $(0.10 + 2y) \text{ M}$.

$$\begin{array}{l} K_{\text{sp}} = [\text{Mg}^{2+}][\text{F}^{-}]^2 = 6.4 \times 10^{-9} \\ (y)(0.10 + 2y)^2 = 6.4 \times 10^{-9} \end{array}$$

Very little MgF_2 dissolves, so y is small. This suggests that $2y \ll 0.10$, so $0.10 + 2y \approx 0.10$. Then

$$(y)(0.10)^2 = 6.4 \times 10^{-9} \quad \text{and} \quad y = 6.4 \times 10^{-7}$$

molar solubility of MgF_2 in 0.10 M NaF = $6.4 \times 10^{-7} \text{ M}$

- (c) The ratio of molar solubility in water to molar solubility in 0.10 M NaF solution is

$$\frac{\text{molar solubility (in H}_2\text{O)}}{\text{molar solubility (in NaF solution)}} = \frac{1.2 \times 10^{-3} \text{ M}}{6.4 \times 10^{-7} \text{ M}} = \frac{1900}{1}$$

The molar solubility of MgF_2 in 0.10 M NaF ($6.4 \times 10^{-7} \text{ M}$) is about 1900 times less than it is in pure water ($1.2 \times 10^{-3} \text{ M}$).

You should now work Exercises 20 and 26.

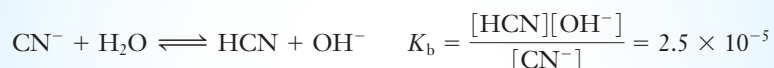
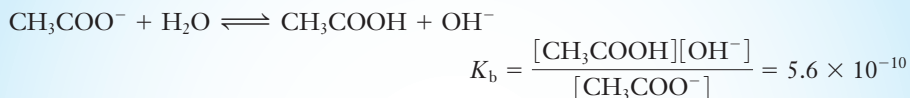
STOP & THINK

When the same ion is produced by a soluble and a slightly soluble salt, the amount from the slightly soluble salt can be neglected.

ENRICHMENT

The Effects of Hydrolysis on Solubility

In Section 18-8 we discussed the hydrolysis of anions of weak acids. For example, we found that for CH_3COO^- and CN^- ions,



We see that K_b for CN^- , the anion of a *very* weak acid, is much larger than K_b for CH_3COO^- , the anion of a much stronger acid. This tells us that in solutions of the same concentration, CN^- ions hydrolyze to a much greater extent than do CH_3COO^- ions. So we might expect that hydrolysis would have a much greater effect on the solubilities of cyanides such as AgCN than on the solubilities of acetates such as AgCH_3COO . It does.

Hydrolysis reduces the concentrations of anions of weak acids, such as F^- , CO_3^{2-} , CH_3COO^- , and CN^- , so its effect must be taken into account when we do very precise solubility calculations. Taking into account the effect of hydrolysis on solubilities of slightly soluble compounds is beyond the scope of this chapter, however.

The Reaction Quotient in Precipitation Reactions

Another application of the solubility product principle is the calculation of the maximum concentrations of ions that can coexist in solution. From these calculations, we can determine whether a **precipitate** will form in a given solution. The reaction quotient, Q (see Section 17-4), is useful in such decisions. We compare Q_{sp} with K_{sp} .

If $Q_{\text{sp}} < K_{\text{sp}}$	Forward process is favored
If $Q_{\text{sp}} = K_{\text{sp}}$	No precipitation occurs; if solid is present, more solid can dissolve
If $Q_{\text{sp}} > K_{\text{sp}}$	Solution is <i>just</i> saturated
	Solid and solution are in equilibrium; neither forward nor reverse process is favored
	Reverse process is favored
	Precipitation occurs to form more solid

EXAMPLE 20-5 Predicting Precipitate Formation

If 100. mL of 0.00075 *M* sodium sulfate, Na_2SO_4 , is mixed with 50. mL of 0.015 *M* barium chloride, BaCl_2 , will a precipitate form?

Plan

We are mixing solutions of two soluble ionic salts. First we find the amount of each solute at the instant of mixing. Next we find the molarity of each solute *at the instant of mixing*. Then we find the concentration of each ion in the *new* solution. Now we ask the question “*Could* any combination of the ions in this solution form a slightly soluble compound?” We consider the kinds of compounds mixed and determine whether a reaction could occur. Both Na_2SO_4 and BaCl_2 are soluble ionic salts. At the moment of mixing, the new solution contains a mixture of Na^+ , SO_4^{2-} , Ba^{2+} , and Cl^- ions. We must consider the possibility of forming two new compounds, NaCl and BaSO_4 .

STOP & THINK

Recall that the reaction quotient has the same algebraic form as the equilibrium constant, except that the concentrations in Q are not necessarily equilibrium concentrations. Remember also that solids do not appear in the expression for K_{sp} or for Q_{sp} .

- Sodium chloride is a soluble ionic compound, so Na^+ and Cl^- do not combine to produce a precipitate in dilute aqueous solutions.
- BaSO_4 , however, is only very slightly soluble, so the answer is “Yes, Ba^{2+} and SO_4^{2-} *might* form BaSO_4 .” We calculate Q_{sp} and compare it with K_{sp} to determine whether solid BaSO_4 is formed.

Solution

We find the *amount* of each solute at the instant of mixing.

$$\underline{\hspace{1cm}} \text{ mmol Na}_2\text{SO}_4 = 100. \text{ mL} \times \frac{0.00075 \text{ mmol Na}_2\text{SO}_4}{\text{mL}} = 0.075 \text{ mmol Na}_2\text{SO}_4$$

$$\underline{\hspace{1cm}} \text{ mmol BaCl}_2 = 50. \text{ mL} \times \frac{0.015 \text{ mmol BaCl}_2}{\text{mL}} = 0.75 \text{ mmol BaCl}_2$$

When *dilute* aqueous solutions are mixed, their volumes can be added to give the volume of the resulting solution.

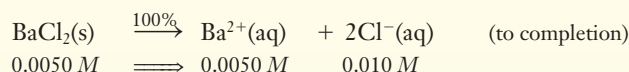
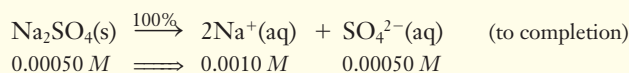
$$\text{volume of mixed solution} = 100. \text{ mL} + 50. \text{ mL} = 150. \text{ mL}$$

Then we find the *molarity of each solute at the instant of mixing*.

$$M_{\text{Na}_2\text{SO}_4} = \frac{0.075 \text{ mmol Na}_2\text{SO}_4}{150. \text{ mL}} = 0.00050 \text{ M Na}_2\text{SO}_4$$

$$M_{\text{BaCl}_2} = \frac{0.75 \text{ mmol BaCl}_2}{150. \text{ mL}} = 0.0050 \text{ M BaCl}_2$$

Now we find the *concentration of each ion* in the new solution.



Solid BaSO_4 will precipitate from the solution *if* $Q_{\text{sp}} > K_{\text{sp}}$ for BaSO_4 . K_{sp} for BaSO_4 is 1.1×10^{-10} . Substituting $[\text{Ba}^{2+}] = 0.0050 \text{ M}$ and $[\text{SO}_4^{2-}] = 0.00050 \text{ M}$ into the Q_{sp} expression for BaSO_4 , we get

$$Q_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (5.0 \times 10^{-3})(5.0 \times 10^{-4}) = 2.5 \times 10^{-6} \quad (Q_{\text{sp}} > K_{\text{sp}})$$

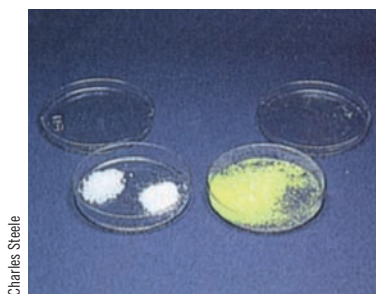
Because $Q_{\text{sp}} > K_{\text{sp}}$, solid BaSO_4 will precipitate until $[\text{Ba}^{2+}][\text{SO}_4^{2-}]$ just equals K_{sp} for BaSO_4 .

You should now work Exercises 28 and 30.

STOP & THINK

Recall that molarity can be expressed as mol/L or as mmol/mL. Because the amounts of dissolved ions in this problem are so small, it is convenient to express molarity as mmol/mL.

► Recall that Q has the same form as the equilibrium constant, in this case K_{sp} , but the concentrations are not necessarily equilibrium concentrations.



Materials can also react in the solid state. When white solid potassium iodide, KI, and white solid lead(II) nitrate, $\text{Pb}(\text{NO}_3)_2$, are ground together, some yellow lead(II) iodide, PbI_2 , forms.

Problem-Solving Tip Detection of Precipitates

The human eye is not a very sensitive detection device. As a rule of thumb, a precipitate can be seen with the naked eye if $Q_{\text{sp}} > K_{\text{sp}}$ by a factor of 1000. In Example 20-5,

Q_{sp} exceeds K_{sp} by a factor of $\frac{2.5 \times 10^{-6}}{1.1 \times 10^{-10}} = 2.3 \times 10^4 = 23,000$. We expect to be able to see the BaSO_4 precipitate that is formed. Modern techniques enable us to detect smaller amounts of precipitates.

EXAMPLE 20-6 Initiation of Precipitation

What $[\text{Ba}^{2+}]$ is necessary to start the precipitation of BaSO_4 in a solution that is 0.0015 M in Na_2SO_4 ? Assume that the Ba^{2+} comes from addition of a solid soluble ionic compound such as BaCl_2 . For BaSO_4 , $K_{\text{sp}} = 1.1 \times 10^{-10}$.

Plan

These are the compounds in Example 20-5. We should recognize that Na_2SO_4 is a soluble ionic compound and that the molarity of SO_4^{2-} is equal to the molarity of the Na_2SO_4 solution. We are given K_{sp} for BaSO_4 , so we solve for $[\text{Ba}^{2+}]$.

Solution

Because Na_2SO_4 is a soluble ionic compound, we know that $[\text{SO}_4^{2-}] = 0.0015\text{ M}$. We can use K_{sp} for BaSO_4 to calculate the $[\text{Ba}^{2+}]$ required for Q_{sp} to just equal K_{sp} .

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$$

$$[\text{Ba}^{2+}] = \frac{1.1 \times 10^{-10}}{[\text{SO}_4^{2-}]} = \frac{1.1 \times 10^{-10}}{1.5 \times 10^{-3}} = 7.3 \times 10^{-8}\text{ M}$$

Addition of enough BaCl_2 to give a barium ion concentration of $7.3 \times 10^{-8}\text{ M}$ just satisfies K_{sp} for BaSO_4 ; that is, $Q_{\text{sp}} = K_{\text{sp}}$. Ever so slightly more BaCl_2 would be required for Q_{sp} to exceed K_{sp} and for precipitation of BaSO_4 to occur. Therefore

$$[\text{Ba}^{2+}] > 7.3 \times 10^{-8}\text{ M} \quad (\text{to initiate precipitation of } \text{BaSO}_4)$$

You should now work Exercise 29.

STOP & THINK

For a 1:1 salt, the following qualitative check can be made. We can take the square root of the BaSO_4 K_{sp} value to get the solution concentrations of the Ba^{2+} and SO_4^{2-} ions for a saturated solution: $[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] \approx 1 \times 10^{-5}\text{ M}$. Because the $[\text{SO}_4^{2-}]$ from the Na_2SO_4 is just over two orders of magnitude larger than this ($1.5 \times 10^{-3}\text{ M}$), the common ion concept should tell us that the $[\text{Ba}^{2+}]$ needs to be just over two orders of magnitude smaller (less than $1 \times 10^{-7}\text{ M}$).

Often we wish to remove an ion from solution by forming an insoluble compound (as in water purification). We use K_{sp} values to calculate the concentrations of ions remaining in solution *after* precipitation has occurred.

EXAMPLE 20-7 Concentration of Common Ion

Suppose we wish to recover silver from an aqueous solution that contains a soluble silver compound such as AgNO_3 by precipitating insoluble silver chloride, AgCl . A soluble ionic compound such as NaCl can be used as a source of Cl^- . What is the minimum concentration of chloride ion needed to reduce the dissolved silver ion concentration to a maximum of $1.0 \times 10^{-9}\text{ M}$? For AgCl , $K_{\text{sp}} = 1.8 \times 10^{-10}$.

Plan

We are given K_{sp} for AgCl and the required equilibrium $[\text{Ag}^+]$, so we solve for $[\text{Cl}^-]$.

Solution

The equations for the reaction of interest and the K_{sp} for AgCl are



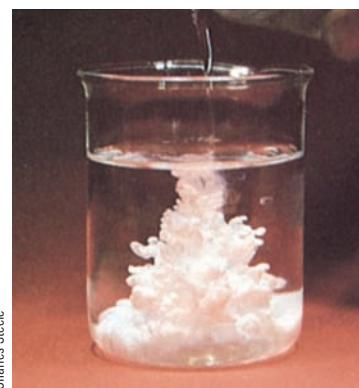
To determine the $[\text{Cl}^-]$ required to reduce the $[\text{Ag}^+]$ to $1.0 \times 10^{-9}\text{ M}$, we solve the K_{sp} expression for $[\text{Cl}^-]$.

$$[\text{Cl}^-] = \frac{1.8 \times 10^{-10}}{[\text{Ag}^+]} = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-9}} = 0.18\text{ M Cl}^-$$

To reduce the $[\text{Ag}^+]$ to $1.0 \times 10^{-9}\text{ M}$ ($0.00000011\text{ g Ag}^+/\text{L}$), NaCl would be added until $[\text{Cl}^-] = 0.18\text{ M}$ in the solution.

You should now work Exercise 32.

► The recovery of silver from the solutions used in developing and fixing black-and-white photographic film and prints presents just such a problem. Silver is an expensive metal, and the recovery is profitable. Moreover, if not recovered, the silver ions would constitute an undesirable pollutant in water supplies.



Charles Steele

Silver chloride precipitates when chloride ions are added to a solution containing silver ions.

► Cations such as Na^+ or K^+ are also present in this solution as spectator ions necessary to balance charge.

STOP & THINK

Because these compounds all have the same 1:1 ion ratio, we can directly compare the relative K_{sp} values and the solubilities of these compounds.

► NaCl , NaBr , NaI , AgNO_3 , and NaNO_3 are soluble compounds that are completely dissociated in dilute aqueous solution. Thus, we do not use or need them in this problem.

► We ignore the extremely small change in volume caused by addition of solid AgNO_3 .

► We are not suggesting that a $1.5 \times 10^{-13} \text{ M}$ solution of AgNO_3 be added. We are pointing out the fact that when sufficient AgNO_3 has been added to the solution to make $[\text{Ag}^+] > 1.5 \times 10^{-13} \text{ M}$, AgI begins to precipitate.

20-4 Fractional Precipitation; $Q_{\text{sp}} \geq K_{\text{sp}}$

We sometimes wish to remove selected ions from solution while leaving others with similar properties in solution. This separation process is called **fractional precipitation**. Consider a solution that contains Cl^- , Br^- , and I^- ions. These halide ions are anions of elements in the same family in the periodic table. Although we expect them to have some similar properties, there are some differences in the solubility products for the silver halides:

Compound	Solubility Product
AgCl	1.8×10^{-10}
AgBr	3.3×10^{-13}
AgI	1.5×10^{-16}

These K_{sp} values show that AgI is less soluble than AgBr and that AgBr is less soluble than AgCl . Silver fluoride is quite soluble in water. This is the expected trend based on the weaker interactions between water molecules and the larger halide anions that have their charge spread out over a larger surface area. This reduces the ability of the water molecules to solvate and pull the larger anions away from the solid.

EXAMPLE 20-8 Concentration Required to Initiate Precipitation

Solid silver nitrate is slowly added to a solution that is 0.0010 M each in NaCl , NaBr , and NaI . Calculate the $[\text{Ag}^+]$ required to initiate the precipitation of each of the silver halides. For AgI , $K_{\text{sp}} = 1.5 \times 10^{-16}$; for AgBr , $K_{\text{sp}} = 3.3 \times 10^{-13}$; and for AgCl , $K_{\text{sp}} = 1.8 \times 10^{-10}$.

Plan

We are given a solution that contains equal concentrations of Cl^- , Br^- , and I^- ions, all of which form insoluble silver salts. Then we slowly add Ag^+ ions. We use each K_{sp} to determine the $[\text{Ag}^+]$ that must be exceeded to initiate precipitation of each salt as we did in Example 20-6.

Solution

We calculate the $[\text{Ag}^+]$ necessary to begin to precipitate each of the silver halides. The solubility product for AgI is

$$[\text{Ag}^+][\text{I}^-] = 1.5 \times 10^{-16}$$

$[\text{I}^-] = 1.0 \times 10^{-3} \text{ M}$, so the $[\text{Ag}^+]$ that must be exceeded to start precipitation of AgI is

$$[\text{Ag}^+] = \frac{1.5 \times 10^{-16}}{[\text{I}^-]} = \frac{1.5 \times 10^{-16}}{1.0 \times 10^{-3}} = 1.5 \times 10^{-13} \text{ M}$$

Therefore, AgI will begin to precipitate when $[\text{Ag}^+] > 1.5 \times 10^{-13} \text{ M}$.

Repeating this kind of calculation for silver bromide gives

$$[\text{Ag}^+][\text{Br}^-] = 3.3 \times 10^{-13}$$

$$[\text{Ag}^+] = \frac{3.3 \times 10^{-13}}{[\text{Br}^-]} = \frac{3.3 \times 10^{-13}}{1.0 \times 10^{-3}} = 3.3 \times 10^{-10} \text{ M}$$

Thus, $[\text{Ag}^+] > 3.3 \times 10^{-10} \text{ M}$ is needed to start precipitation of AgBr .

For the precipitation of silver chloride to begin,

$$[\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[\text{Ag}^+] = \frac{1.8 \times 10^{-10}}{[\text{Cl}^-]} = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-3}} = 1.8 \times 10^{-7} \text{ M}$$

To precipitate AgCl , we must have $[\text{Ag}^+] > 1.8 \times 10^{-7} \text{ M}$.

Problem-Solving Tip

Because of the simple 1:1 ion ratio, it is quite easy to estimate and check the answer without a calculator. The square root of the $\text{AgI } K_{sp}$ value (simplified to 1×10^{-16}) gives $[\text{Ag}^+] = [\text{I}^-] \approx 1 \times 10^{-8} \text{ M}$. The initial $[\text{I}^-]$ from the added NaI is $1 \times 10^{-3} \text{ M}$, which is five orders of magnitude larger. The common ion concept and 1:1 ion ratio tell us that the $[\text{Ag}^+]$ needed to initiate precipitation should be five orders of magnitude smaller than $1 \times 10^{-8} \text{ M}$, or about $1 \times 10^{-13} \text{ M}$.

Similar estimations can be made for the AgBr and AgCl calculations to check their answers. The AgBr example is a little more complicated due to the odd power on the K_{sp} value (3.3×10^{-13}) that cannot simply be divided by two to estimate the square root of the power of 10. Changing this to 33×10^{-14} simplifies estimating the square root as approximately $6 \times 10^{-7} \approx [\text{Ag}^+] = [\text{Br}^-]$. The initial $[\text{Br}^-] = 1 \times 10^{-3} \text{ M}$, which is a little more than three orders of magnitude larger than $6 \times 10^{-7} \text{ M}$. Thus, the $[\text{Ag}^+]$ to initiate precipitation should be a little over three orders of magnitude smaller, or about $1 \times 10^{-10} \text{ M}$.

This calculation tells us that when AgNO_3 is added slowly to a solution that is 0.0010 M in each of NaI , NaBr , and NaCl , AgI precipitates first, AgBr precipitates second, and AgCl precipitates last.

We can also calculate the fraction of one salt that precipitates before another salt begins to form in a fractional precipitation experiment.

► As AgNO_3 is added to the solution containing Cl^- , Br^- , and I^- ions, some AgBr and AgCl may precipitate *locally*. As the solution is stirred, AgBr and AgCl redissolve as long as $[\text{Ag}^+]$ is not large enough to exceed their K_{sp} values in the *bulk* of the solution.

EXAMPLE 20-9 Fractional Precipitation

Refer to Example 20-8. (a) Calculate the percentage of I^- precipitated before AgBr precipitates. (b) Calculate the percentages of I^- and Br^- precipitated before Cl^- precipitates.

Plan

From Example 20-8 we know the $[\text{Ag}^+]$ that must be exceeded to initiate precipitation of each of three silver halides, AgI , AgBr , and AgCl . We use each of these values of $[\text{Ag}^+]$ with the appropriate K_{sp} expression, in turn, to find the concentration of each halide ion that remains in solution (unprecipitated). We express these halide ion concentrations as percent unprecipitated. Then we subtract each from exactly 100% to find the percentage of each halide that precipitates.

Solution

- (a) In Example 20-8 we found that AgBr begins to precipitate when $[\text{Ag}^+] > 3.3 \times 10^{-10} \text{ M}$. This value for $[\text{Ag}^+]$ can be substituted into the K_{sp} expression for AgI to determine $[\text{I}^-]$ remaining *unprecipitated* when AgBr begins to precipitate.

$$[\text{Ag}^+][\text{I}^-] = 1.5 \times 10^{-16}$$

$$[\text{I}^-]_{\text{unppt'd}} = \frac{1.5 \times 10^{-16}}{[\text{Ag}^+]} = \frac{1.5 \times 10^{-16}}{3.3 \times 10^{-10}} = 4.5 \times 10^{-7} \text{ M}$$

The percentage of I^- unprecipitated is

$$\% \text{I}^-_{\text{unppt'd}} = \frac{[\text{I}^-]_{\text{unppt'd}}}{[\text{I}^-]_{\text{orig}}} \times 100\% = \frac{4.5 \times 10^{-7} \text{ M}}{1.0 \times 10^{-3} \text{ M}} \times 100\%$$

$$= 0.045\% \text{I}^- \text{ unprecipitated}$$

Therefore, 99.955% of the I^- precipitates *before* AgBr begins to precipitate.

- (b) Similar calculations show that *just before* AgCl begins to precipitate, $[\text{Ag}^+] = 1.8 \times 10^{-7} \text{ M}$, and the $[\text{I}^-]$ unprecipitated is calculated as in Part (a).

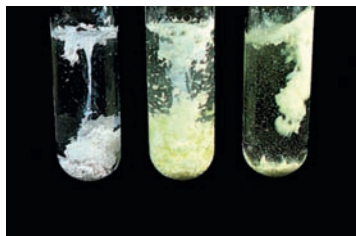
$$[\text{Ag}^+][\text{I}^-] = 1.5 \times 10^{-16}$$

$$[\text{I}^-]_{\text{unppt'd}} = \frac{1.5 \times 10^{-16}}{[\text{Ag}^+]} = \frac{1.5 \times 10^{-16}}{1.8 \times 10^{-7}} = 8.3 \times 10^{-10} \text{ M}$$

► In Example 20-7 we did a similar calculation, but we did not express the result in terms of the percentage of an ion precipitated.

► We have subtracted 0.045% from *exactly* 100%. We have therefore *not* violated the rules for significant figures.

Charles Steele



Freshly precipitated AgCl is white (*left*), AgBr is very pale yellow (*center*), and AgI is yellow (*right*). Polarizabilities of these halide ions increase in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$. Colors of the silver halides become more intense in the same direction. Solubilities of the silver halides increase in the opposite direction.

The percentage of I^- unprecipitated just before AgCl precipitates is

$$\begin{aligned}\% \text{I}^-_{\text{unppt'd}} &= \frac{[\text{I}^-]_{\text{unppt'd}}}{[\text{I}^-]_{\text{orig}}} \times 100\% = \frac{8.3 \times 10^{-10} M}{1.0 \times 10^{-3} M} \times 100\% \\ &= 0.000083\% \text{I}^- \text{ unprecipitated}\end{aligned}$$

Therefore, 99.999917% of the I^- precipitates before AgCl begins to precipitate.

A similar calculation for the amount of Br^- precipitated just before AgCl begins to precipitate gives

$$\begin{aligned}[\text{Ag}^+][\text{Br}^-] &= 3.3 \times 10^{-13} \\ [\text{Br}^-]_{\text{unppt'd}} &= \frac{3.3 \times 10^{-13}}{[\text{Ag}^+]} = \frac{3.3 \times 10^{-13}}{1.8 \times 10^{-7}} = 1.8 \times 10^{-6} M \\ \% \text{Br}^-_{\text{unppt'd}} &= \frac{[\text{Br}^-]_{\text{unppt'd}}}{[\text{Br}^-]_{\text{orig}}} \times 100\% = \frac{1.8 \times 10^{-6} M}{1.0 \times 10^{-3} M} \times 100\% \\ &= 0.18\% \text{Br}^- \text{ unprecipitated}\end{aligned}$$

Thus, 99.82% of the Br^- precipitates before AgCl begins to precipitate.

You should now work Exercises 36 and 38.

We have described the precipitation reactions that occur when solid AgNO_3 is added slowly to a solution that is $0.0010 M$ in Cl^- , Br^- , and I^- . Silver iodide begins to precipitate first; 99.955% of the I^- precipitates before any solid AgBr is formed. Silver bromide begins to precipitate next; 99.82% of the Br^- and 99.999917% of the I^- precipitate before any solid AgCl forms. This shows that we can separate these ions very effectively by fractional precipitation.

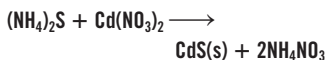
20-5 Simultaneous Equilibria Involving Slightly Soluble Compounds

Many weak acids and bases react with many metal ions to form insoluble compounds. In such cases, we must take into account the weak acid or weak base equilibrium as well as the solubility equilibrium. The most common examples involve the reaction of metal ions with aqueous ammonia to form insoluble metal hydroxides.

James W. Morganthaler



Pouring ammonium sulfide solution into a solution of cadmium nitrate gives a precipitate of cadmium sulfide.



Cadmium sulfide is used as a pigment in artists' oil-based paints.

EXAMPLE 20-10 Simultaneous Equilibria

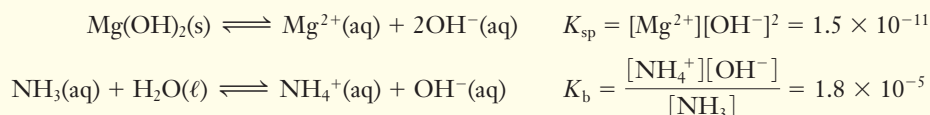
We make a solution that is $0.10 M$ in magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, and $0.10 M$ in aqueous ammonia, a weak base. Will magnesium hydroxide, $\text{Mg}(\text{OH})_2$, precipitate from this solution? K_{sp} for $\text{Mg}(\text{OH})_2$ is 1.5×10^{-11} , and K_{b} for aqueous NH_3 is 1.8×10^{-5} .

Plan

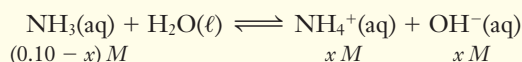
We first write equations for the two *reversible* reactions and their equilibrium constant expressions. We note that $[\text{OH}^-]$ appears in both equilibrium constant expressions. From the statement of the problem, we know the concentration of Mg^{2+} . We use the K_{b} expression for aqueous NH_3 to find $[\text{OH}^-]$. Then we calculate Q_{sp} for $\text{Mg}(\text{OH})_2$ and compare it with its K_{sp} .

Solution

Two equilibria and their equilibrium constant expressions must be considered.



The $[\text{OH}^-]$ in 0.10 M aqueous NH_3 is calculated as in Example 18-14.



$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.10 - x)} \quad ; \quad x = 1.3 \times 10^{-3} M = [\text{OH}^-]$$

Magnesium nitrate is a soluble ionic compound, so $[\text{Mg}^{2+}] = 0.10 M$. Now that both $[\text{Mg}^{2+}]$ and $[\text{OH}^-]$ are known, we calculate Q_{sp} for $\text{Mg}(\text{OH})_2$.

$$[\text{Mg}^{2+}][\text{OH}^-]^2 = Q_{\text{sp}}$$

$$(0.10)(1.3 \times 10^{-3})^2 = 1.7 \times 10^{-7} = Q_{\text{sp}}$$

$K_{\text{sp}} = 1.5 \times 10^{-11}$, so we see that $Q_{\text{sp}} > K_{\text{sp}}$.

Therefore, $\text{Mg}(\text{OH})_2$ would precipitate, lowering $[\text{Mg}^{2+}]$ and $[\text{OH}^-]$ until $Q_{\text{sp}} = K_{\text{sp}}$.

You should now work Exercise 46.

Example 20-11 shows how we can calculate the concentration of weak base that is required to initiate precipitation of an insoluble metal hydroxide.

EXAMPLE 20-11 Simultaneous Equilibria

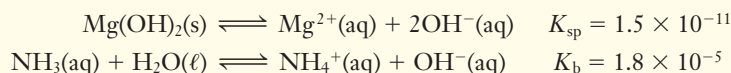
What concentration of aqueous ammonia is necessary to just start precipitation of $\text{Mg}(\text{OH})_2$ from a 0.10 M solution of $\text{Mg}(\text{NO}_3)_2$? Refer to Example 20-10.

Plan

We have the same reactions and equilibrium constant expressions as in Example 20-10. We are given $[\text{Mg}^{2+}]$, so we use the K_{sp} expression of $\text{Mg}(\text{OH})_2$ to calculate the $[\text{OH}^-]$ necessary to initiate precipitation. Then we find the molarity of aqueous NH_3 solution that would furnish the desired $[\text{OH}^-]$.

Solution

Two equilibria and their equilibrium constant expressions must be considered.



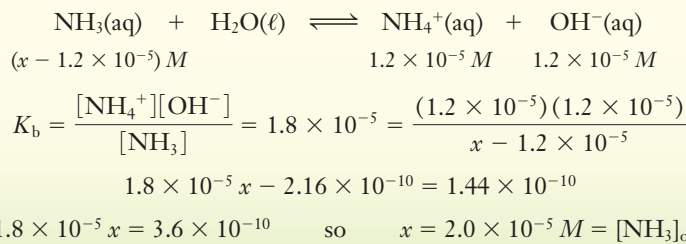
We find the $[\text{OH}^-]$ necessary to initiate precipitation of $\text{Mg}(\text{OH})_2$ when $[\text{Mg}^{2+}] = 0.10 M$.

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.5 \times 10^{-11}$$

$$[\text{OH}^-]^2 = \frac{1.5 \times 10^{-11}}{[\text{Mg}^{2+}]} = \frac{1.5 \times 10^{-11}}{0.10} = 1.5 \times 10^{-10} \quad [\text{OH}^-] = 1.2 \times 10^{-5} M$$

Therefore, $[\text{OH}^-] > 1.2 \times 10^{-5} M$ to initiate precipitation of $\text{Mg}(\text{OH})_2$.

Now we use the equilibrium of NH_3 as a weak base to find the $[\text{NH}_3]$ that will produce $1.2 \times 10^{-5} M \text{ OH}^-$. Let x be the *original* $[\text{NH}_3]$.



The solution must be ever so slightly greater than $2.0 \times 10^{-5} M$ in NH_3 to initiate precipitation of $\text{Mg}(\text{OH})_2$ in a 0.10 M solution of $\text{Mg}(\text{NO}_3)_2$.

STOP & THINK

We have calculated the $[\text{OH}^-]$ produced by the ionization of 0.10 M aqueous NH_3 . This is the equilibrium concentration of OH^- in this solution. There is no reason to double this value when we put it into the K_{sp} expression! But we do need to raise it to the coefficient power of 2 in the $\text{Mg}(\text{OH})_2$ equilibrium expression.

STOP & THINK

Remember that x represents the *original* concentration of the weak base NH_3 . The small value of K_{b} tells us that 1.2×10^{-5} and x are of comparable magnitude, so neither can be disregarded in the term $(x - 1.2 \times 10^{-5})$.

A solution that contains a weak base can be buffered (by addition of a salt of the weak base) to decrease its basicity. Significant concentrations of some metal ions that form insoluble hydroxides can be kept in such solutions, as Example 20-12 illustrates.

EXAMPLE 20-12 Simultaneous Equilibria

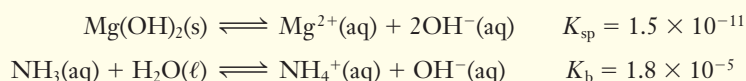
What minimum number of moles of NH_4Cl must be added to 1.0 liter of solution that is 0.10 M in $\text{Mg}(\text{NO}_3)_2$ and 0.10 M in NH_3 to prevent precipitation of $\text{Mg}(\text{OH})_2$?

Plan

These are the same compounds, in the same concentrations, that we used in Example 20-10. Because we know $[\text{Mg}^{2+}]$, we must find the maximum $[\text{OH}^-]$ that can exist in the solution *without exceeding* K_{sp} for $\text{Mg}(\text{OH})_2$. Then we find the minimum concentration of NH_4Cl that is necessary to buffer the NH_3 solution to keep the $[\text{OH}^-]$ below this calculated value.

Solution

The buffering action of NH_4Cl in the presence of NH_3 decreases the concentration of OH^- . Again we have two equilibria.



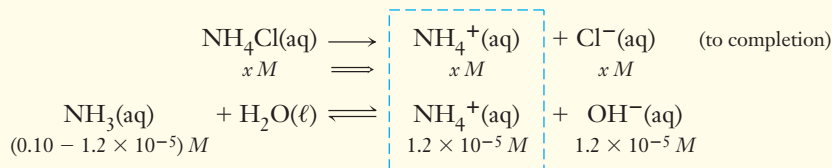
To find the *maximum* $[\text{OH}^-]$ that can exist in solution *without causing precipitation*, we substitute $[\text{Mg}^{2+}]$ into the K_{sp} for $\text{Mg}(\text{OH})_2$.

$$[\text{Mg}^{2+}][\text{OH}^-]^2 = 1.5 \times 10^{-11}$$

$$[\text{OH}^-]^2 = \frac{1.5 \times 10^{-11}}{[\text{Mg}^{2+}]} = \frac{1.5 \times 10^{-11}}{0.10} = 1.5 \times 10^{-10}$$

$$[\text{OH}^-] = 1.2 \times 10^{-5} M \quad (\text{maximum } [\text{OH}^-] \text{ possible})$$

To prevent precipitation of $\text{Mg}(\text{OH})_2$ in *this* solution, $[\text{OH}^-]$ must be equal to or less than $1.2 \times 10^{-5} M$. We can use K_{b} for aqueous NH_3 to calculate the number of moles of NH_4Cl necessary to buffer 1.0 L of 0.10 M aqueous NH_3 so that $[\text{OH}^-] = 1.2 \times 10^{-5} M$. Let x = number of mol/L of NH_4Cl required.



We can assume that $(x + 1.2 \times 10^{-5}) \approx x$ and $(0.10 - 1.2 \times 10^{-5}) \approx 0.10$.

$$\frac{(x)(1.2 \times 10^{-5})}{0.10} = 1.8 \times 10^{-5}$$

$$x = 0.15 \text{ mol of } \text{NH}_4^+ \text{ per liter of solution}$$

Addition of at least 0.15 mol of NH_4Cl to 1.0 L of 0.10 M aqueous NH_3 decreases $[\text{OH}^-]$ to $1.2 \times 10^{-5} M$ or lower. Then K_{sp} for $\text{Mg}(\text{OH})_2$ is not exceeded in this solution, and so no precipitate would form.

You should now work Exercises 42 and 44.

► In Example 20-10, we found that $\text{Mg}(\text{OH})_2$ will precipitate from a solution that is 0.10 M in $\text{Mg}(\text{NO}_3)_2$ and 0.10 M in NH_3 .

► You may wish to refer to Example 19-6 to refresh your understanding of buffer solutions.

STOP & THINK

$x = 0.15 M \text{ NH}_4^+$ confirms that the approximation of $x + 1.2 \times 10^{-5} \approx x$ used above to simplify the algebra was a good one.

Examples 20-10, 20-11, and 20-12 illustrate a very important point.

All relevant equilibria must be satisfied when more than one equilibrium is required to describe a solution.

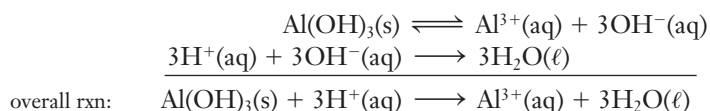
20-6 Dissolving Precipitates; $Q_{sp} < K_{sp}$

A precipitate dissolves when the concentrations of its ions are reduced so that K_{sp} is no longer exceeded, that is, when $Q_{sp} < K_{sp}$. The precipitate then dissolves until $Q_{sp} = K_{sp}$. Precipitates can be dissolved by several types of reactions. All involve removing ions from solution.

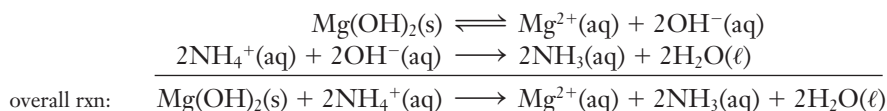
Converting an Ion to a Weak Electrolyte

Three specific illustrations follow.

1. *Converting OH^- to H_2O .* Insoluble $Al(OH)_3$ dissolves in acids. H^+ ions react with OH^- ions [from the saturated $Al(OH)_3$ solution] to form the weak electrolyte H_2O . This makes $Q_{sp} = [Al^{3+}][OH^-]^3 < K_{sp}$, so that the dissolution equilibrium shifts to the right and $Al(OH)_3$ dissolves.

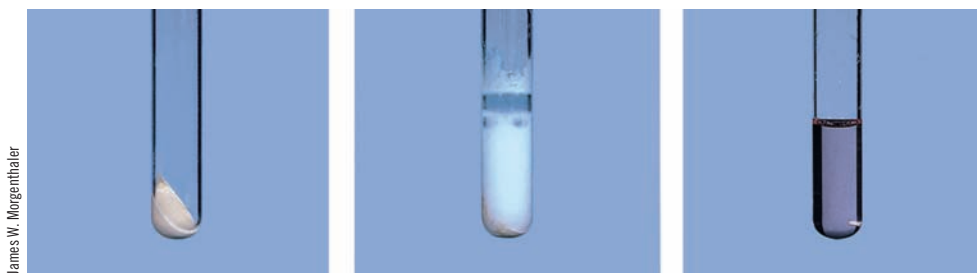
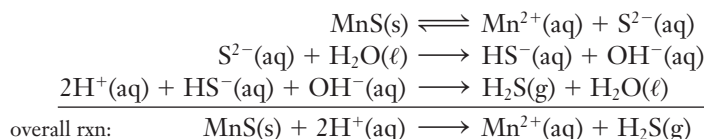


2. *Converting NH_4^+ to NH_3 .* Ammonium ions, from a salt such as NH_4Cl , dissolve insoluble $Mg(OH)_2$. The NH_4^+ ions combine with OH^- ions in the saturated $Mg(OH)_2$ solution. This forms the weak electrolytes NH_3 and H_2O . The result is that $Q_{sp} = [Mg^{2+}][OH^-]^2 < K_{sp}$, and so the $Mg(OH)_2$ dissolves.



This process, dissolution of $Mg(OH)_2$ in an NH_4Cl solution, is the reverse of the reaction we considered in Example 20-10. There, $Mg(OH)_2$ precipitated from a solution of aqueous NH_3 .

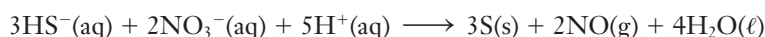
3. *Converting S^{2-} to H_2S .* Nonoxidizing acids dissolve most insoluble metal sulfides. For example, 6 M HCl dissolves MnS . The H^+ ions combine with S^{2-} ions to form H_2S , a gas that bubbles out of the solution. The result is that $Q_{sp} = [Mn^{2+}][S^{2-}] < K_{sp}$, and so the MnS dissolves.



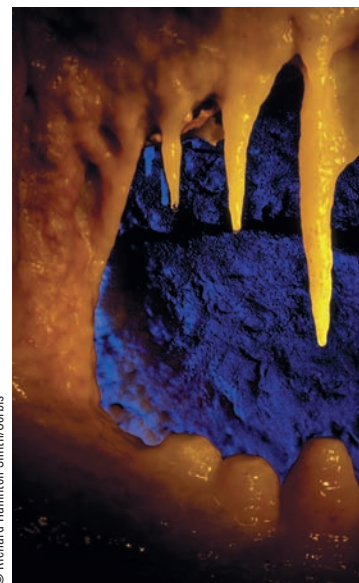
Manganese(II) sulfide, MnS , is salmon-colored. MnS dissolves in 6 M HCl . The resulting solution of $MnCl_2$ is pale pink.

Converting an Ion to Another Species by a Redox Reaction

Most insoluble metal sulfides dissolve in hot dilute HNO_3 because NO_3^- ions oxidize S^{2-} ions, or actually their hydrolysis product (HS^-), to elemental sulfur. This removes HS^- (and thus S^{2-}) ions from the solution and promotes the dissolving of more of the metal sulfide.



► Solubility product constants, like other equilibrium constants, are thermodynamic quantities. They tell us about the extent to which a given reaction can occur, but nothing about how fast that reaction occurs.



© Richard Hamilton Smith/Corbis

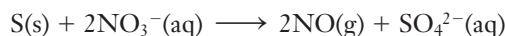
Stalactite and stalagmite formations in limestone caves result from the dissolution and reprecipitation of calcium carbonate, $CaCO_3$.

STOP & THINK
 S^{2-} , like O^{2-} , does not exist in appreciable amounts in aqueous solutions. This is because it is basic enough to react with H_2O to produce HS^- and OH^- , as shown in the second reaction in part 3.

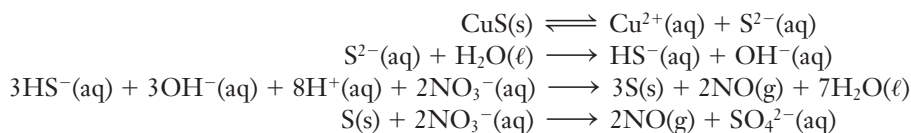
► It is sometimes convenient to ignore hydrolysis of S^{2-} ions in aqueous solutions. Leaving out the hydrolysis step may give the false impression that S^{2-} ions exist in solution. The overall net ionic equation for this redox reaction will be the same, however, with or without consideration of hydrolysis of the S^{2-} ions.

Unless otherwise noted, all content on this page is © Cengage Learning.

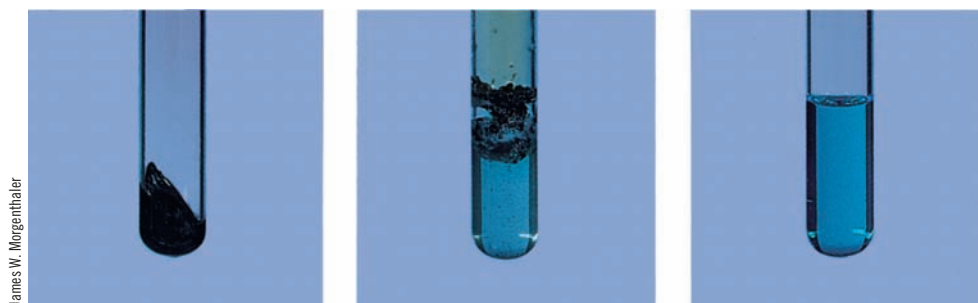
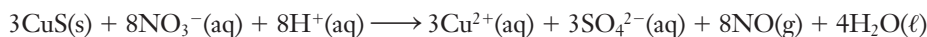
The elemental sulfur produced usually reacts with more HNO_3 to make H_2SO_4 via the following reaction.



Consider copper(II) sulfide, CuS , in equilibrium with its ions. This equilibrium lies far to the left. Removal of the S^{2-} or HS^- ions by oxidation to SO_4^{2-} favors the reaction to the right, and so CuS(s) dissolves in hot dilute HNO_3 .



Multiply the first, second, and fourth equations by 3, and then add and cancel like terms to give the net ionic equation for dissolving CuS(s) in hot dilute HNO_3 .

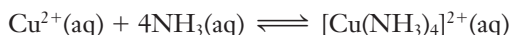


Copper(II) sulfide, CuS , is black. As CuS dissolves in 6 M HNO_3 , some NO is oxidized to brown NO_2 by O_2 in the air. The resulting solution of Cu^{2+} ions (SO_4^{2-} and NO_3^- counter anions) is blue.

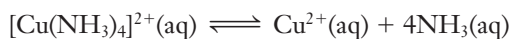
Complex Ion Formation

The cations in many slightly soluble compounds can form *complex ions*. This often results in dissolution of the slightly soluble compound. Some metal ions share electron pairs donated by molecules and ions such as NH_3 , CN^- , OH^- , F^- , Cl^- , Br^- , and I^- to form coordinate covalent bonds to metal ions. Coordinate covalent bonds are formed as these electron-donating groups (ligands) replace H_2O molecules from hydrated metal ions. The decrease in the concentration of the hydrated metal ion shifts the solubility equilibrium to the right.

Many copper(II) compounds react with excess aqueous NH_3 to form the deep-blue complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$.



The dissociation of this complex ion is represented as



The equilibrium constant for the dissociation of a complex ion is called its **dissociation constant**, K_d .

$$K_d = \frac{[\text{Cu}^{2+}][\text{NH}_3]^4}{[[\text{Cu}(\text{NH}_3)_4]^{2+}]} = 8.5 \times 10^{-13}$$

Recall that $\text{Cu}^{2+}(\text{aq})$ is really a hydrated ion, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. The preceding reaction and its K_d expression are represented more accurately as



$$K_d = \frac{[[\text{Cu}(\text{H}_2\text{O})_6]^{2+}][\text{NH}_3]^4}{[[\text{Cu}(\text{NH}_3)_4]^{2+}]} = 8.5 \times 10^{-13}$$

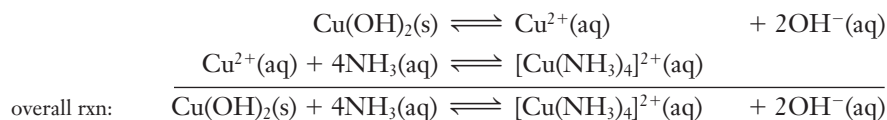
The more effectively a ligand competes with H_2O for a coordination site on the metal ions, the smaller K_d is. This tells us that in a comparison of complexes with the same num-

► “Ligand” is the name given to an atom or a group of atoms bonded to the metal center in complex ions. Ligands are Lewis bases.

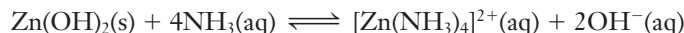
► As before, the outer brackets mean molar concentrations. The inner brackets are part of the formula of the complex ion.

ber of ligands, the smaller the K_d value, the more stable the complex ion. Some complex ions and their dissociation constants, K_d , are listed in Appendix I.

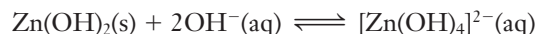
Copper(II) hydroxide dissolves in an excess of aqueous NH_3 to form the deep-blue complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$. This decreases the $[\text{Cu}^{2+}]$ so that $Q_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^-]^2 < K_{\text{sp}}$, and so the $\text{Cu}(\text{OH})_2$ dissolves.



Similarly, $\text{Zn}(\text{OH})_2$ dissolves in excess NH_3 to form $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ions.

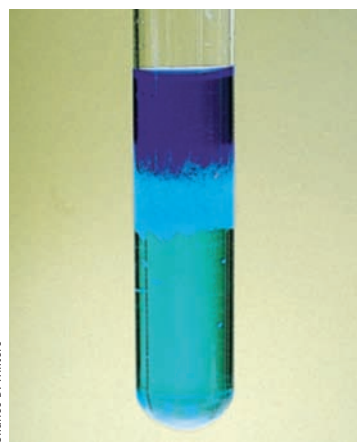


Amphoteric hydroxides such as $\text{Zn}(\text{OH})_2$ also dissolve in excess strong base by forming complex ions (Section 10-6).



We see that we are able to shift equilibria (in this case, to dissolve $\text{Zn}(\text{OH})_2$) by taking advantage of complex ion formation.

► For brevity, we often omit H_2O from formulas of hydrated ions. For example, we write $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ as Cu^{2+} or $\text{Cu}^{2+}(\text{aq})$.



Charles D. Winters

Concentrated aqueous NH_3 was added *slowly* to a solution of copper(II) sulfate, CuSO_4 . Unreacted blue copper(II) sulfate solution remains in the bottom part of the test tube. The light-blue precipitate in the middle is copper(II) hydroxide, $\text{Cu}(\text{OH})_2$. The top layer contains deep-blue $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ions that were formed as some $\text{Cu}(\text{OH})_2$ dissolved in excess aqueous NH_3 .

KEY TERMS

Common ion effect Suppression of ionization of a weak electrolyte by the presence in the same solution of a strong electrolyte containing one of the same ions as the weak electrolyte.

Complex ions Ions resulting from the formation of coordinate covalent bonds between simple cations and other ions or molecules (ligands).

Dissociation constant (K_d) The equilibrium constant that applies to the dissociation of a complex ion into a simple ion and coordinating species (ligands).

Fractional precipitation Removal of some ions from solution by precipitation while leaving other ions, with similar properties, in solution.

Molar solubility The number of moles of a solute that dissolve to produce a liter of saturated solution.

Precipitate A solid formed by mixing in solution the constituent ions of a slightly soluble compound.

Reaction quotient (in precipitation reactions) (Q_{sp}) The mass action expression that applies to the dissolution of a slightly soluble compound; this has the same algebraic form as that for K_{sp} , except that the concentrations are *not necessarily* equilibrium ones.

Solubility product constant (K_{sp}) The equilibrium constant that applies to the dissolution of a slightly soluble compound.

Solubility product principle The solubility product constant expression for a slightly soluble compound is the product of the concentrations of the constituent ions, each raised to the power that corresponds to the number of ions in one formula unit.

Unless otherwise noted, all content on this page is © Cengage Learning.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Solubility Product

1. The solubility product constant values listed in Appendix H were determined at 25°C. How would those K_{sp} values change, if at all, with a change in temperature?
2. State the solubility product principle. What is its significance?
3. Why do we not include a term for the solid in a solubility product expression?
4. What do we mean when we refer to the molar solubility of a compound?
5. Write the solubility product expression for each of the following salts: (a) MgF_2 ; (b) $AlPO_4$; (c) $CuCO_3$; (d) Ag_3PO_4 .
6. Write the solubility product expression for each of the following salts: (a) $Mn_3(AsO_4)_2$; (b) Hg_2I_2 [contains diatomic mercury(I) ions, Hg_2^{2+}]; (c) AuI_3 ; (d) $SrCO_3$.
7. ● ▲ The K_{sp} value for $BaSO_4$ is calculated from the expression $K_{sp} = [Ba^{2+}][SO_4^{2-}]$, whereas the K_{sp} value for $Mg(OH)_2$ is calculated from the expression, $K_{sp} = [Mg^{2+}][OH^-]^2$. Explain why the hydroxide ion concentration is squared, but none of the other concentrations are squared.

13. ▲ Calculate the K_{sp} for zinc phosphate if 1.18×10^{-4} grams of zinc phosphate dissolved to make 2.5 liters of a saturated solution.

Uses of Solubility Product Constants

14. Seashells are calcium carbonate with traces of colored impurities. The solubility product for calcium carbonate is 4.8×10^{-9} . What is the solubility of calcium carbonate in grams per liter of solution?



Charles D. Winters

Experimental Determination of K_{sp}

Values of K_{sp} calculated from the solubility data in these exercises may not agree exactly with the solubility products given in Appendix H because of rounding differences.

8. From the solubility data given for the following compounds, calculate their solubility product constants.
 - (a) $SrCrO_4$, strontium chromate, 1.2 mg/mL
 - (b) BiI_3 , bismuth iodide, 7.7×10^{-3} g/L
 - (c) $Fe(OH)_2$, iron(II) hydroxide, 1.1×10^{-3} g/L
 - (d) SnI_2 , tin(II) iodide, 10.9 g/L
9. From the solubility data given for the following compounds, calculate their solubility product constants.
 - (a) $CuBr$, copper(I) bromide, 1.0×10^{-3} g/L
 - (b) AgI , silver iodide, 2.8×10^{-8} g/10 mL
 - (c) $Pb_3(PO_4)_2$, lead(II) phosphate, 6.2×10^{-7} g/L
 - (d) Ag_2SO_4 , silver sulfate, 5.0 mg/mL
10. Construct a table like Table 20-1 for the compounds listed in Exercise 8. Which compound has (a) the highest molar solubility, (b) the lowest molar solubility, (c) the largest K_{sp} , (d) the smallest K_{sp} ?
11. Construct a table like Table 20-1 for the compounds listed in Exercise 9. Which compound has (a) the highest molar solubility, (b) the lowest molar solubility, (c) the largest K_{sp} , (d) the smallest K_{sp} ?
12. A solution is produced by stirring 1.1000 gram of calcium fluoride in 1.00 liter of water at 25°C. Careful analysis shows that 0.0163 grams of calcium fluoride has dissolved. Calculate the K_{sp} for calcium fluoride based on these data.

15. Calculate molar solubilities, concentrations of constituent ions, and solubilities in grams per liter for the following compounds at 25°C: (a) $Cd(CN)_2$, cadmium cyanide; (b) PbI_2 , lead iodide; (c) $Sr_3(AsO_4)_2$, strontium arsenate; (d) Hg_2CO_3 , mercury(I) carbonate [the formula for the mercury(I) ion is Hg_2^{2+}].
16. Calculate molar solubilities, concentrations of constituent ions, and solubilities in grams per liter for the following compounds at 25°C: (a) $CuCl$, copper(I) chloride; (b) $Ba_3(PO_4)_2$, barium phosphate; (c) PbF_2 , lead(II) fluoride; (d) $Sr_3(PO_4)_2$, strontium phosphate.
17. What is the concentration of lead ions in one liter of saturated $PbCrO_4$ solution?
18. Barium sulfate is used to produce distinct X-rays of the gastrointestinal tract. What is the maximum mass of barium sulfate that can dissolve in 5.00 liters of water (a volume much greater than that of the average gastrointestinal tract)?
19. Calculate the molar solubility of $CuBr$ in 0.010 M KBr solution.
20. Calculate the molar solubility of Ag_2SO_4 in 0.12 M K_2SO_4 solution.
21. Construct a table similar to Table 20-1 for the compounds listed in Exercise 15. Which compound has (a) the highest molar solubility; (b) the lowest molar solubility; (c) the

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

- highest solubility, expressed in grams per liter; (d) the lowest solubility, expressed in grams per liter?
22. Construct a table similar to Table 20-1 for the compounds listed in Exercise 16. Which compound has (a) the highest molar solubility; (b) the lowest molar solubility; (c) the highest solubility, expressed in grams per liter; (d) the lowest solubility, expressed in grams per liter?
 23. Of the three compounds CuCO_3 , Ca(OH)_2 , and Ag_2CrO_4 , which has (a) the highest molar solubility; (b) the lowest molar solubility; (c) the highest solubility, expressed in grams per liter; (d) the lowest solubility, expressed in grams per liter?
 24. Of the three compounds, Ag_2CO_3 , AgCl , and Pb(OH)_2 , which has (a) the highest molar solubility; (b) the lowest molar solubility; (c) the highest solubility, expressed in grams per liter; (d) the lowest solubility, expressed in grams per liter?
 25. What volume of water is required to dissolve 7.5 grams of copper(II) carbonate, CuCO_3 ?
 26. Which has the greater molar solubility in 0.125 M K_2CrO_4 solution: BaCrO_4 or Ag_2CrO_4 ?
 27. Will a precipitate form when 1.00 g of AgNO_3 is added to 50.0 mL of 0.050 M NaCl ? If so, would you expect the precipitate to be visible?
 28. Will a precipitate of PbCl_2 form when 5.0 g of solid $\text{Pb(NO}_3)_2$ is added to 1.00 L of 0.010 M NaCl ? Assume that volume change is negligible.
 29. Sodium bromide and lead nitrate are soluble in water. Will lead bromide precipitate when 1.03 g of NaBr and 0.332 g of $\text{Pb(NO}_3)_2$ are dissolved in sufficient water to make 1.00 L of solution?
 30. Will a precipitate of Cu(OH)_2 form when 10.0 mL of 0.010 M NaOH is added to 1.00 L of 0.010 M CuCl_2 ?
 31. A solution is 0.0100 M in Pb^{2+} ions. If 0.103 mol of solid Na_2SO_4 is added to 1.00 L of this solution (with negligible volume change), what percentage of the Pb^{2+} ions remain in solution?
 32. A solution is 0.0100 M in Pb^{2+} ions. If 0.103 mol of solid NaI is added to 1.00 L of this solution (with negligible volume change), what percentage of the Pb^{2+} ions remain in solution?
 33. ▲ A solution is 0.0100 M in $\text{Ba(NO}_3)_2$. If 0.103 mol of solid Na_3PO_4 is added to 1.00 L of this solution (with negligible volume change), what percentage of the Ba^{2+} ions remain in solution?
- What percentage of the Au^+ has precipitated at this point? (c) Calculate $[\text{Au}^+]$ and $[\text{Ag}^+]$ when CuBr just begins to precipitate.
37. ▲ A solution is 0.020 M in Pb^{2+} and 0.020 M in Ag^+ . As Cl^- is introduced to the solution by the addition of solid NaCl , determine (a) which substance will precipitate first, AgCl or PbCl_2 , and (b) the fraction of the metal ion in the first precipitate that remains in solution at the moment the precipitation of the second compound begins.
 38. A solution is 0.050 M in K_2SO_4 and 0.050 M in K_2CrO_4 . Solid $\text{Pb(NO}_3)_2$ is added slowly without changing the volume appreciably. (a) Which salt, PbSO_4 or PbCrO_4 , will precipitate first? (b) What is $[\text{Pb}^{2+}]$ when the salt in part (a) begins to precipitate? (c) What is $[\text{Pb}^{2+}]$ when the other lead salt begins to precipitate? (d) What are $[\text{SO}_4^{2-}]$ and $[\text{CrO}_4^{2-}]$ when the lead salt in part (c) begins to precipitate?
 39. Solid $\text{Pb(NO}_3)_2$ is added slowly to a solution that is 0.015 M each in NaOH , K_2CO_3 , and Na_2SO_4 . (a) In what order will solid Pb(OH)_2 , PbCO_3 , and PbSO_4 begin to precipitate? (b) Calculate the percentages of OH^- and CO_3^{2-} that have precipitated when PbSO_4 begins to precipitate.
 40. Suppose you have three beakers that contain, respectively, 100 mL of each of the following solutions: (i) 0.0015 M KOH , (ii) 0.0015 M K_2CO_3 , (iii) 0.0015 M KCN . (a) If solid zinc nitrate, $\text{Zn(NO}_3)_2$, were added slowly to each beaker, what concentration of Zn^{2+} would be required to initiate precipitation? (b) If solid zinc nitrate were added to each beaker until $[\text{Zn}^{2+}] = 0.0015 \text{ M}$, what concentrations of OH^- , CO_3^{2-} , and CN^- would remain in solution, that is, unprecipitated? Neglect any volume change when solid is added.
 41. ▲ Suppose you have three beakers that contain, respectively, 100 mL each of the following solutions: (i) 0.0015 M KOH , (ii) 0.0015 M K_2CO_3 , (iii) 0.0015 M KI . (a) If solid lead nitrate, $\text{Pb(NO}_3)_2$, were added slowly to each beaker, what concentration of Pb^{2+} would be required to initiate precipitation? (b) If solid lead nitrate were added to each beaker until $[\text{Pb}^{2+}] = 0.0015 \text{ M}$, what concentrations of OH^- , CO_3^{2-} , and I^- would remain in solution, that is, unprecipitated? Neglect any volume change when solid is added.

Fractional Precipitation

34. ● What is fractional precipitation?
35. ▲ Solid Na_2SO_4 is added slowly to a solution that is 0.10 M in $\text{Pb(NO}_3)_2$ and 0.10 M in $\text{Ba(NO}_3)_2$. In what order will solid PbSO_4 and BaSO_4 form? Calculate the percentage of Ba^{2+} that precipitates just before PbSO_4 begins to precipitate.
36. ▲ To a solution that is 0.010 M in Cu^+ , 0.010 M in Ag^+ , and 0.010 M in Au^+ , solid NaBr is added slowly. Assume that there is no volume change due to the addition of solid NaBr . (a) Which compound will begin to precipitate first? (b) Calculate $[\text{Au}^+]$ when AgBr just begins to precipitate.

Simultaneous Equilibria

42. ▲ If a solution is made 0.080 M in $\text{Mg(NO}_3)_2$, 0.075 M in aqueous ammonia, and 3.5 M in NH_4NO_3 , will Mg(OH)_2 precipitate? What is the pH of this solution?
43. ▲ If a solution is made 0.090 M in $\text{Mg(NO}_3)_2$, 0.090 M in aqueous ammonia, and 0.080 M in NH_4NO_3 , will Mg(OH)_2 precipitate? What is the pH of this solution?
44. ▲ Calculate the solubility of CaF_2 in a solution that is buffered at $[\text{H}^+] = 0.0050 \text{ M}$ with $[\text{HF}] = 0.10 \text{ M}$.
45. ▲ Calculate the solubility of AgCN in a solution that is buffered at $[\text{H}^+] = 0.000200 \text{ M}$, with $[\text{HCN}] = 0.01 \text{ M}$.



46. If a solution is $2.0 \times 10^{-5} M$ in $Mn(NO_3)_2$ and $1.0 \times 10^{-3} M$ in aqueous ammonia, will $Mn(OH)_2$ precipitate?
47. ▲ If a solution is $0.040 M$ in manganese(II) nitrate, $Mn(NO_3)_2$, and $0.080 M$ in aqueous ammonia, will manganese(II) hydroxide, $Mn(OH)_2$, precipitate?
48. Milk of magnesia is a suspension of the slightly soluble compound $Mg(OH)_2$ in water. (a) What is the molar solubility of $Mg(OH)_2$ in a $0.015 M$ NaOH solution? (b) What is the molar solubility of $Mg(OH)_2$ in a $0.015 M$ $MgCl_2$ solution?



Charles D. Winters

Milk of magnesia

49. How many moles of $Cr(OH)_3$ will dissolve in 555 mL of a solution with a pH of 5.00?
50. Determine whether a precipitate forms when a $0.00050 M$ solution of magnesium nitrate is brought to a pH of 8.70.
51. ▲ What concentration of NH_4NO_3 is necessary to prevent precipitation of $Mn(OH)_2$ in the solution of Exercise 47?
52. (a) What is the pH of a saturated solution of $Fe(OH)_2$? (b) What is the solubility in grams of $Fe(OH)_2/100. mL$ of solution?
53. (a) What is the pH of a saturated solution of $Cu(OH)_2$? (b) What is the solubility in grams of $Cu(OH)_2/100. mL$ of solution?
54. What is the maximum concentration of Zn^{2+} in a solution of pH 10.00?
55. A solution contains the metal ions listed below, all at the same concentration. The addition of thioacetamide, CH_3CSNH_2 , produces sulfide ion, S^{2-} , causing the ions to precipitate as the sulfides. Each sulfide begins to precipitate at a different concentration of sulfide ion. As the concentration of sulfide ion increases (starting from 0), in what order will the metal sulfides precipitate? (Which one will start to precipitate first, second, third, and fourth?)
- | | |
|----------------------------|--|
| iron(II) ion, Fe^{2+} | $K_{sp} = 4.9 \times 10^{-18}$ for FeS |
| lead(II) ion, Pb^{2+} | $K_{sp} = 8.4 \times 10^{-28}$ for PbS |
| mercury(II) ion, Hg^{2+} | $K_{sp} = 3.0 \times 10^{-53}$ for HgS |
| tin(II) ion, Sn^{2+} | $K_{sp} = 1.0 \times 10^{-28}$ for SnS |
56. If a solution is $4.3 \times 10^{-4} M$ in magnesium nitrate, $Mg(NO_3)_2$, and $5.2 \times 10^{-2} M$ in aqueous ammonia, NH_3 , will $Mg(OH)_2$ precipitate? ($K_{sp} = 1.5 \times 10^{-11}$ for $Mg(OH)_2$, $K_b = 1.8 \times 10^{-5}$ for NH_3)

Dissolution of Precipitates and Complex Ion Formation

57. You will often work with salts of Fe^{3+} , Pb^{2+} , and Al^{3+} in the laboratory. (All are found in nature, and all are important economically.) If you have a solution containing these three ions, each at a concentration of $0.10 M$, what is the order in which their hydroxides precipitate as aqueous NaOH is slowly added to the solution?
58. ● Explain, by writing appropriate equations, how the following insoluble compounds can be dissolved by the addition of a solution of nitric acid. (Carbonates dissolve in strong acids to form water and gaseous carbon dioxide.) What is the “driving force” for each reaction? (a) $Cu(OH)_2$; (b) $Sn(OH)_4$; (c) $ZnCO_3$; (d) $(PbOH)_2CO_3$.
59. ● Explain, by writing equations, how the following insoluble compounds can be dissolved by the addition of a solution of ammonium nitrate or ammonium chloride. (a) $Mg(OH)_2$; (b) $Mn(OH)_2$; (c) $Ni(OH)_2$.
60. ● The following insoluble sulfides can be dissolved in $3.0 M$ hydrochloric acid. Explain how this is possible, and write the appropriate equations. (a) MnS ; (b) CuS .
61. ● The following sulfides are less soluble than those listed in Exercise 60 and can be dissolved in hot $6.0 M$ nitric acid, an oxidizing acid. Explain how, and write the appropriate balanced equations. (a) PbS ; (b) CuS ; (c) Bi_2S_3 .
62. ● Why would MnS be expected to be more soluble in $0.10 M$ HCl solution than in water? Would the same be true for $Mn(NO_3)_2$?
63. ● ▲ For each pair, choose the salt that would be expected to be more soluble in acidic solution than in pure water, and justify your choice. (a) $Hg_2(CH_3COO)_2$ or Hg_2Br_2 ; (b) $Pb(OH)_2$ or PbI_2 ; (c) AgI or $AgNO_3$.

Mixed Exercises

64. We mix 25.0 mL of a $0.0030 M$ solution of $BaCl_2$ and 50.0 mL of a $0.050 M$ solution of NaF. (a) Find $[Ba^{2+}]$ and $[F^-]$ in the mixed solution at the instant of mixing (before any possible reaction occurs). (b) Would BaF_2 precipitate?
65. ▲ A concentrated, strong acid is added to a solid mixture of 0.025-mol samples of $Fe(OH)_2$ and $Cu(OH)_2$ placed in 1.0 L of water. At what values of pH will the dissolution of each hydroxide be complete? (Assume negligible volume change.)
66. A solution is $0.015 M$ in I^- ions and $0.015 M$ in Br^- ions. Ag^+ ions are introduced to the solution by the addition of solid $AgNO_3$. Determine (a) which compound will precipitate first, AgI or $AgBr$, and (b) the percentage of the halide ion in the first precipitate that is removed from solution before precipitation of the second compound begins.
67. Calculate the molar solubility of Ag_2SO_4 (a) in pure water, (b) in $0.010 M$ $AgNO_3$, and (c) in $0.010 M$ K_2SO_4 .
68. Barium and all of its compounds are very toxic. For example, the estimated fatal dose of barium chloride ($BaCl_2$, solubility 375 g/L) is about 1 gram for a 70-kg human. Yet the barium contrast agent used in abdominal studies contains 450 grams of barium sulfate ($BaSO_4$, solubility $0.00246 g/L$). Why would the use of barium

carbonate (BaCO_3 , solubility 0.02 g/L) as a contrast agent be tragic?

69. Solid sodium carbonate, Na_2CO_3 , is added to a solution that is 0.0326 M in strontium nitrate, $\text{Sr}(\text{NO}_3)_2$, and 0.0270 M in barium nitrate, $\text{Ba}(\text{NO}_3)_2$. Calculate the percentage of strontium that has precipitated as strontium carbonate, SrCO_3 , just before barium carbonate, BaCO_3 , begins to precipitate. (K_{sp} : $\text{SrCO}_3 = 9.4 \times 10^{-10}$, $\text{BaCO}_3 = 8.1 \times 10^{-9}$)

Conceptual Exercises

70. In each of the following cases, decide whether a precipitate will form when mixing the indicated reagents, and write a balanced equation for the reaction.
 (a) $\text{Na}_2\text{SO}_4(\text{aq}) + \text{Mg}(\text{NO}_3)_2(\text{aq})$
 (b) $\text{K}_3\text{PO}_4(\text{aq}) + \text{FeCl}_3(\text{aq})$
71. (a) Are “insoluble” substances really insoluble? (b) What do we mean when we refer to insoluble substances?
72. Solubility product calculations are actually based on heterogeneous equilibria. Why are pure solids and liquids exempted from these calculations?
73. Draw a picture of a portion of a saturated silver chloride solution at the molecular level. Show a small amount of solid plus some dissociated ions. You need not show water or waters of hydration. Prepare a second drawing that includes the same volume of solution, but twice as much solid. Should your drawing include more, fewer, or the same number of silver ions?
74. The solubility product constants of silver chloride, AgCl , and silver chromate, Ag_2CrO_4 , are 1.8×10^{-10} and 9.0×10^{-12} , respectively. Suppose that the chloride, $\text{Cl}^-(\text{aq})$, and chromate, $\text{CrO}_4^{2-}(\text{aq})$, ions are both present in the same solution at concentrations of 0.010 M each. A standard solution of silver ions, $\text{Ag}^+(\text{aq})$, is dispensed slowly from a buret into this solution while it is stirred vigorously. Solid silver chloride is white, and silver chromate is red. What will be the concentration of $\text{Cl}^-(\text{aq})$ ions in the mixture when the first tint of red color appears in the mixture?
75. Calculate the solubility of silver bromide, AgBr , in moles per liter, in pure water. Compare this value with the molar solubility of AgBr in 225 mL of water to which 0.15 g of NaBr has been added.
77. The solubility product principle is generally valid only for saturated solutions in which the total concentration of ions of the slightly soluble compound is no more than about 0.01 M. Compounds with a K_{sp} less than 10^{-40} have extremely low solubility. Examine the table of solubility product constants in Appendix H. Which compound appears to be the most soluble? Calculate its molar solubility. Which compound appears to be the least soluble? Calculate its molar solubility.
78. A 1.00-L solution contains 0.010 M F^- and 0.010 M SO_4^{2-} . Solid barium nitrate is slowly added to the solution.
 (a) Calculate the $[\text{Ba}^{2+}]$ when BaSO_4 begins to precipitate.
 (b) Calculate the $[\text{Ba}^{2+}]$ when BaF_2 starts to precipitate. Assume no volume change occurs. K_{sp} values: $\text{BaSO}_4 = 1.1 \times 10^{-11}$, $\text{BaF}_2 = 1.7 \times 10^{-6}$.
79. How many moles of CO_3^{2-} must be added to 0.75 liter of a 0.10 M Sr^{2+} solution to produce a solution that is 1.0×10^{-6} M Sr^{2+} ? How many moles of CO_3^{2-} are in the final solution, and how many moles of CO_3^{2-} are in the precipitate formed? Assume no volume change for the solution.
80. A fluoridated water supply contains 1 mg/L of F^- . What is the maximum amount of Ca^{2+} , expressed in grams per liter, that can exist in this water supply?
81. Many industrial operations require very large amounts of water as a coolant in heat exchange processes. Muddy or cloudy water is usually unsatisfactory because the dispersed solids may clog filters or deposit sediment in pipes and pumps. Murky water can be clarified on a large scale by adding agents to coagulate colloidal material, and then allowing the resulting solid to settle out in holding tanks or ponds before the clarified water is sent to plant intakes. Recent methods employ the addition of both calcium hydroxide and magnesium carbonate. If 56 g of $\text{Ca}(\text{OH})_2$ and 45 g of MgCO_3 were added to 520. liters of water, would these compounds form a precipitate of calcium carbonate?
82. Magnesium carbonate is used in the manufacture of a high-density *magnesite* brick. This material is not well suited to general exterior use because the magnesium carbonate easily erodes. What percentage of 28 grams of surface-exposed MgCO_3 would be lost through the solvent action of 15 liters of water? Assume sufficient contact time for the water to become saturated with MgCO_3 .

Building Your Knowledge

76. In the calculation of the molar solubility of a compound such as lead(II) chloride, PbCl_2 , given its solubility product constant, K_{sp} , the concentration of the chloride ion, Cl^- , is exactly twice the concentration of the lead(II) ion, Pb^{2+} . In the solubility product constant expression, this “doubled” concentration is also squared. However, when lead(II) chloride is precipitated by the combining of solutions of lead(II) nitrate, $\text{Pb}(\text{NO}_3)_2$, and potassium chloride, KCl , the concentration of the chloride ion is not doubled before it is squared. Explain this difference.

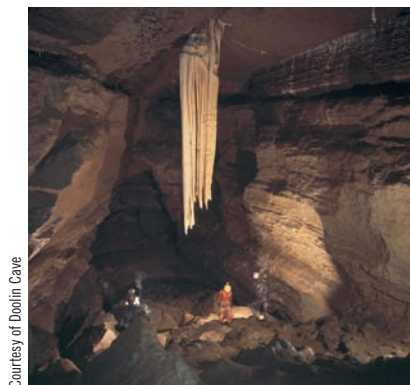
Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

83. Search the web for an application of a relatively insoluble salt as a soil additive.
84. Use the *Handbook of Chemistry and Physics* or other suitable reference to find solubility data for inorganic compounds. What are some qualitative rules that relate to solubilities?



85. Use the *Handbook of Chemistry and Physics* or other suitable reference to find solubility data for inorganic compounds. List five nickel salts that are listed as being insoluble in water but soluble in acid. Write the net ionic equation for the dissolution of each salt in a strong acid solution.
86. ▲ Suppose you had 1.00 L of the mixed halide solution described in Example 20-8. (a) Calculate the mass of solid AgNO_3 that you would need to add to the solution to accomplish the desired separations. (b) The minimum mass that can be weighed with a typical electronic balance is about 0.0001 g. Do you suppose that this would be a practical method to carry out this separation? (c) Can you suggest a more practical approach to this fractional precipitation? Show calculations to assess the practicality of your suggested approach.
87. The 23-foot Great Stalactite in Doolin Cave, County Clare, Ireland (below) has an estimated weight of 10 metric tons (1 metric ton = 1000 kg). Assume that this weight is entirely calcite, CaCO_3 , which has a cold water solubility of 0.0014 g/100 mL, and that the stalactite was formed by simple precipitation from a saturated solution. (a) How many liters of CaCO_3 -saturated water deposited calcite from the cave ceiling to produce this massive formation? (b) From these data, what are the solubility product constant and the molar solubility for calcite?
88. Color change indicators have other uses than to monitor pH. Water-sensitive laboratory chemicals are often stored in the presence of the dessicant “Drierite” (white $\text{CaSO}_4(\text{s})$, which attracts atmospheric water to form white $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). “Indicating Drierite” also contains a small amount of colored $\text{CoCl}_2(\text{s})$, which changes color upon hydration and signals that the storage atmosphere is no longer dry. Look up CoCl_2 and its hydrated salts $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$ in the *CRC Handbook of Chemistry and Physics* or in various sources on the internet. (a) What colors are the “dry” (anhydrous) and “wet” forms of this salt? (b) Is the material in the photo below ready to use as a dessicant?



Courtesy of Doolin Cave

Doolin Cave



Courtesy of W. A. Hammond Drierite Co.

Commercially available indicating Drierite™

Electrochemistry

21



Nellis Air Force Base in Nevada has a giant solar panel power array that generates about 14 megawatts of power for the base. This provides about 25% of the electrical power needs for the base.

U.S. Air Force photo by Airman 1st Class Nadine Y. Barclay

OUTLINE

21-1 Electrical Conduction

21-2 Electrodes

Electrolytic Cells

21-3 The Electrolysis of Molten Sodium Chloride (The Downs Cell)

21-4 The Electrolysis of Aqueous Sodium Chloride

21-5 The Electrolysis of Aqueous Sodium Sulfate

21-6 Counting Electrons: Coulometry and Faraday's Law of Electrolysis

21-7 Commercial Applications of Electrolytic Cells

Voltaic or Galvanic Cells

21-8 The Construction of Simple Voltaic Cells

21-9 The Zinc–Copper Cell

21-10 The Copper–Silver Cell

Standard Electrode Potentials

21-11 The Standard Hydrogen Electrode

21-12 The Zinc–SHE Cell

21-13 The Copper–SHE Cell

21-14 Standard Electrode Potentials

21-15 Uses of Standard Electrode Potentials

21-16 Standard Electrode Potentials for Other Half-Reactions

21-17 Corrosion

21-18 Corrosion Protection

Effect of Concentrations (or Partial Pressures) on Electrode Potentials

21-19 The Nernst Equation

21-20 Using Electrochemical Cells to Determine Concentrations

21-21 The Relationship of E_{cell}^0 to ΔG^0 and K_{eq}

Primary Voltaic Cells

21-22 Dry Cells

Secondary Voltaic Cells

21-23 The Lead Storage Battery

21-24 The Nickel–Cadmium (Nicad) Cell

21-25 The Hydrogen–Oxygen Fuel Cell

Unless otherwise noted, all content on this page is © Cengage Learning.

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Use the terminology of electrochemistry (terms such as “cell,” “electrode,” “cathode,” “anode”)
- ▶ Describe the differences between electrolytic cells and voltaic (galvanic) cells
- ▶ Recognize oxidation and reduction half-reactions, and know at which electrode each occurs for electrolytic cells and for voltaic cells
- ▶ Write half-reactions and overall cell reactions for electrolysis processes
- ▶ Use Faraday’s Law of Electrolysis to calculate amounts of products formed, amounts of current passed, time elapsed, and oxidation state
- ▶ Describe the refining and plating of metals by electrolytic methods
- ▶ Describe the construction of simple voltaic cells from half-cells and a salt bridge, and understand the function of each component
- ▶ Write half-reactions and overall cell reactions for voltaic cells
- ▶ Write and interpret the shorthand notation for voltaic cells
- ▶ Compare various voltaic cells to determine the relative strengths of oxidizing and reducing agents
- ▶ Interpret standard reduction potentials
- ▶ Use standard reduction potentials, E^0 , to calculate the potential of a standard voltaic cell, E_{cell}^0
- ▶ Use standard reduction potentials to identify the cathode and the anode in a standard cell
- ▶ Use standard reduction potentials to predict the spontaneity of a redox reaction
- ▶ Use standard reduction potentials to identify oxidizing and reducing agents in a cell or in a redox reaction
- ▶ Describe some corrosion processes and some methods for preventing corrosion
- ▶ Use the Nernst equation to relate electrode potentials and cell potentials to different concentrations and partial pressures
- ▶ Relate the standard cell potential (E_{cell}^0) to the standard Gibbs free energy change (ΔG^0) and the equilibrium constant (K_{eq})
- ▶ Distinguish between primary and secondary voltaic cells
- ▶ Describe the compositions and reactions of some useful primary and secondary cells (batteries)
- ▶ Describe the electrochemical processes involved in discharging and recharging a lead storage (automobile) battery

Electrochemistry deals with the chemical changes produced by electric current and with the production of electricity by chemical reactions. Many metals are purified or are plated onto jewelry by electrochemical methods. Digital watches, automobile starters, calculators, and pacemakers are just a few devices that depend on electrochemically produced power via batteries. Corrosion of metals is also an electrochemical process.

We learn much about chemical reactions from the study of electrochemistry. The amount of electrical energy consumed or produced can be measured quite accurately. All electrochemical reactions involve the transfer of electrons and are therefore *oxidation–reduction* reactions. The sites of oxidation and reduction are separated physically so that oxidation occurs at one location, and reduction occurs at the other. Electrochemical processes require some method of introducing a stream of electrons into a reacting chemical system and some means of withdrawing electrons. In most applications the reacting system is contained in a **cell**, and an electric current enters or exits by **electrodes**.

We classify electrochemical cells into two types.

1. **Electrolytic cells** are those in which electrical energy from an external source causes *nonspontaneous* chemical reactions to occur.
2. **Voltaic cells** are those in which *spontaneous* chemical reactions produce electricity and supply it to an external circuit.

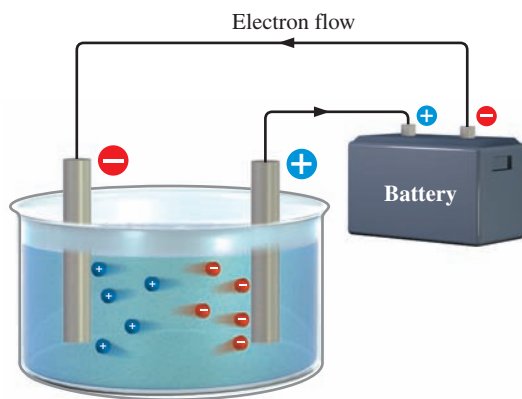


Figure 21-1 The motion of ions through a solution is an electric current. This accounts for ionic (electrolytic) conduction. Positively charged ions migrate toward the negative electrode, and negatively charged ions migrate toward the positive electrode. Here the rate of migration is greatly exaggerated for clarity. The ionic velocities are actually only slightly greater than random molecular speeds.

We will discuss several kinds of electrochemical cells. From experimental observations we deduce what is happening at each electrode and for the overall reaction chemistry. We then construct simplified diagrams of the cells.

21-1 Electrical Conduction

Electric current represents transfer of charge. Charge can be conducted through metals and through pure liquid electrolytes (that is, molten salts) or solutions containing electrolytes. The former type of conduction is called **metallic conduction**. It involves the flow of electrons with no similar movement of the atoms of the metal and no obvious changes in the metal (see Section 13-17). **Ionic**, or **electrolytic, conduction** is the conduction of electric current by the motion of ions through a solution or a pure liquid. Positively charged ions migrate toward the negative electrode, while negatively charged ions move toward the positive electrode. Both kinds of conduction, ionic and metallic, occur in electrochemical cells (Figure 21-1).

► A few organic salts are liquids at room temperature. These are called ionic liquids.

21-2 Electrodes

Electrodes are surfaces on which oxidation or reduction half-reactions occur. They may or may not participate in the reactions. Those that do not react are called **inert electrodes**. Regardless of the kind of cell, electrolytic or voltaic, the electrodes are identified as follows.

The **cathode** is defined as the electrode at which *reduction* occurs as electrons are gained by some species. The **anode** is the electrode at which *oxidation* occurs as electrons are lost by some species.

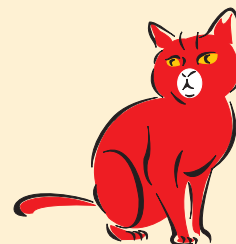
Each of these can be either the positive or the negative electrode depending on the cell type.

Electrolytic Cells

In some electrochemical cells, *nonspontaneous* (reactant-favored) chemical reactions are forced to occur by the input of electrical energy. This process is called **electrolysis**. An electrolytic cell consists of a container for the reaction material with electrodes immersed in the reaction material and connected to a source of direct current. Inert electrodes are often used so that they do not become involved with the reaction.

STOP & THINK

A simple way to remember the name of the electrode that is doing the reduction is to think about a “red cat”—that is, *reduction* always occurs at the cathode.



► *Lysis* means “splitting apart.” In many electrolytic cells, compounds are split into their constituent elements, for example, the splitting of water, H_2O into H_2 and O_2 gases.

Unless otherwise noted, all content on this page is © Cengage Learning.

21-3 The Electrolysis of Molten Sodium Chloride (The Downs Cell)

► Molten NaCl, melting point = 801°C, is a clear, colorless liquid that looks like water.

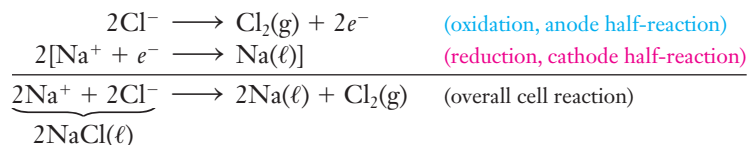
► The Na metal remains liquid because its melting point is only 97.8°C. It floats because it is less dense than the molten NaCl.

► In this chapter, as in Chapters 6 and 11, we often use red type to emphasize reduction and blue type to emphasize oxidation.

Solid sodium chloride does not conduct electricity. Its ions vibrate about fixed positions, but they are not free to move throughout the crystal. Molten (melted) NaCl, however, is an excellent conductor because its ions are freely mobile. Consider a cell in which a source of direct current is connected by wires to two inert graphite electrodes (Figure 21-2a). They are immersed in a container of molten sodium chloride. When the current with a high enough voltage flows, we observe the following.

1. A pale green gas, which is chlorine, Cl_2 , is liberated at one electrode.
2. Molten, silvery-white metallic sodium, Na, forms at the other electrode and floats on top of the molten sodium chloride.

From these observations we can deduce the processes of the cell. Chlorine must be produced by oxidation of Cl^- ions, and the electrode at which this happens must be the anode. Metallic sodium is produced by reduction of Na^+ ions at the cathode, where electrons are being forced into the cell.



The formation of metallic Na and gaseous Cl_2 from NaCl is *nonspontaneous* except at temperatures very much higher than 801°C. The direct current (dc) source must supply electrical energy to force this reaction to occur. Electrons are used in the cathode half-reaction (reduction) and produced in the anode half-reaction (oxidation). They therefore

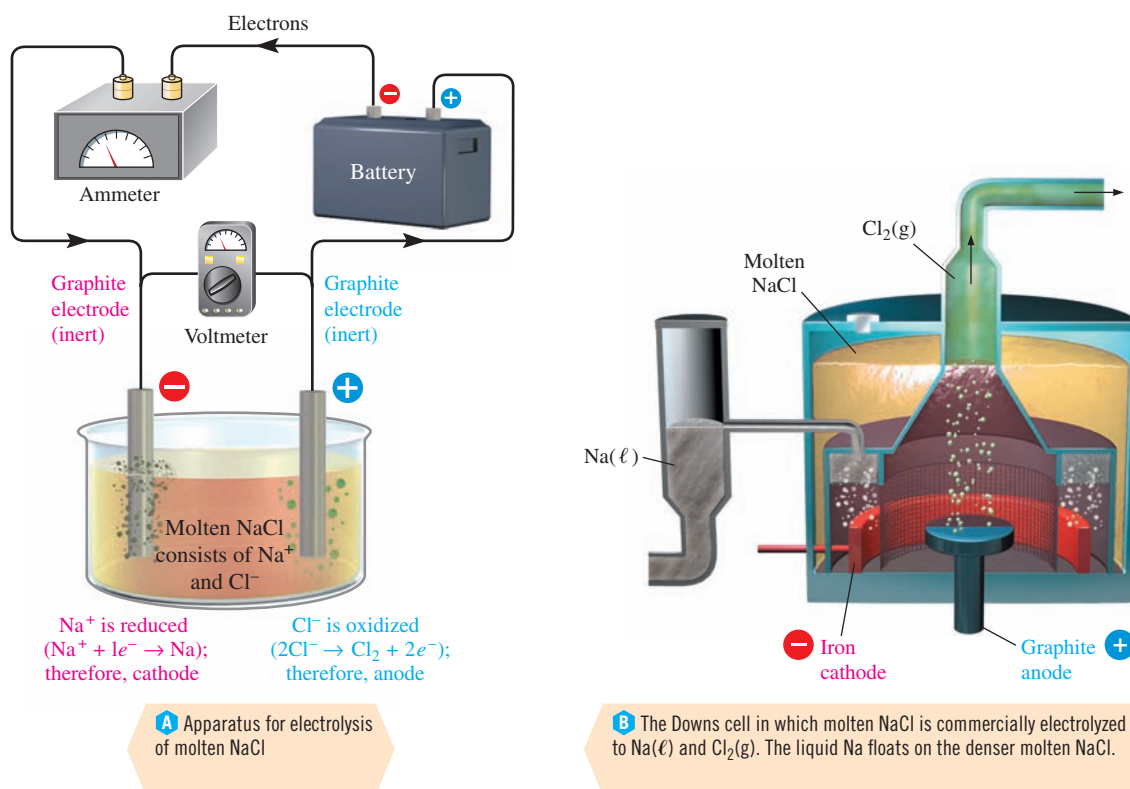


Figure 21-2 Electrolysis of molten sodium chloride, NaCl, to produce $\text{Na}(\ell)$ and $\text{Cl}_2(\text{g})$.

travel through the wire from *anode* to *cathode*. The dc source forces electrons to flow non-spontaneously from the positive electrode to the negative electrode. The anode is the positive electrode and the cathode the negative electrode *in all electrolytic cells*. Figure 21-2a is a simplified diagram of the cell.

Sodium and chlorine must not be allowed to come in contact with each other because they react spontaneously, rapidly, and explosively to form sodium chloride. Figure 21-2b shows the **Downs cell** that is used for the industrial electrolysis of sodium chloride. The Downs cell is expensive to run, mainly because of the cost of construction, the cost of the electricity, and the cost of heating the NaCl to melt it. Nevertheless, electrolysis of a molten sodium salt is the most practical means by which metallic Na can be obtained, owing to its extremely high reactivity. Once liberated by the electrolysis, the liquid Na metal is drained off, cooled, and cast into blocks. These must be stored in an inert environment (e.g., in mineral oil) to prevent reaction with atmospheric O₂ or water.

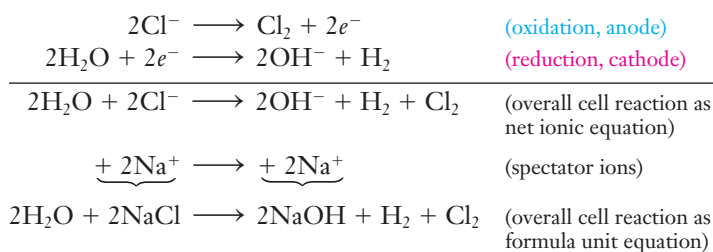
Electrolysis of NaCl in the Downs cell is the main commercial method of producing metallic sodium. The Cl₂ gas produced in the Downs cell is cooled, compressed, and marketed. This partially offsets the expense of producing metallic sodium, but most chlorine is produced by the cheaper electrolysis of aqueous NaCl.

21-4 The Electrolysis of Aqueous Sodium Chloride

Consider the electrolysis of a moderately concentrated solution of NaCl in water, using inert electrodes. The following experimental observations are made when a sufficiently high voltage is applied across the electrodes of a suitable cell.

1. H₂ gas is liberated at one electrode. The solution becomes basic in that vicinity.
2. Cl₂ gas is liberated at the other electrode.

Chloride ions are obviously being oxidized to Cl₂ in this cell, as they were in the electrolysis of molten NaCl. But Na⁺ ions are not reduced to metallic Na. Instead, gaseous H₂ and aqueous OH⁻ ions are produced by reduction of H₂O molecules at the cathode. Water is more easily reduced than Na⁺ ions. This is primarily because the reduction of Na⁺ would produce the very active metal Na, whereas the reduction of H₂O produces the more stable products H₂(g) and OH⁻(aq). The active metals Li, K, Ca, and Na (see Table 6-9) all react with water to produce H₂(g) and the corresponding metal hydroxide [LiOH, KOH, Ca(OH)₂, and NaOH], so we do not expect these metals to be produced in aqueous solution. Later in this chapter (Section 21-14), we learn the quantitative basis for predicting which of several possible oxidations or reductions is favored. The half-reactions and overall cell reaction for this electrolysis are



The cell is illustrated in Figure 21-3. As before, the battery forces the electrons to flow from the anode (+) through the wire to the cathode (-).

The overall cell reaction produces gaseous H₂ and Cl₂ and an aqueous solution of NaOH, called caustic soda. Solid NaOH is then obtained by evaporation of the solution. This is the most important commercial preparation of each of these substances. It is much less expensive than the electrolysis of molten NaCl because it is not necessary to heat the solution to the high temperatures needed to melt NaCl.

► The direction of *spontaneous* flow for negatively charged particles is from negative to positive.

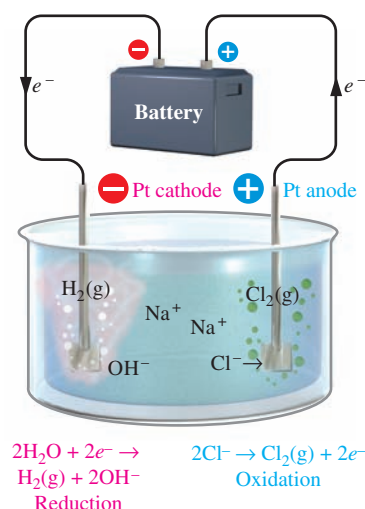


Figure 21-3 Electrolysis of aqueous NaCl solution. Although several reactions occur at both the anode and the cathode, the net result is the production of H₂(g) and NaOH at the cathode and Cl₂(g) at the anode. A few drops of phenolphthalein indicator were added to the solution. The solution turns pink at the cathode, where OH⁻ ions are formed and the solution becomes basic.

► We will omit the notation that indicates states of substances—(s), (ℓ), (g), and (aq)—except where states are not obvious. This is a common shortcut when writing equations.

► Not surprisingly, the fluctuations in commercial prices of these widely used industrial products—H₂, Cl₂, and NaOH—have often paralleled one another.

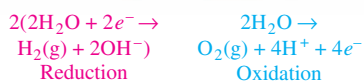
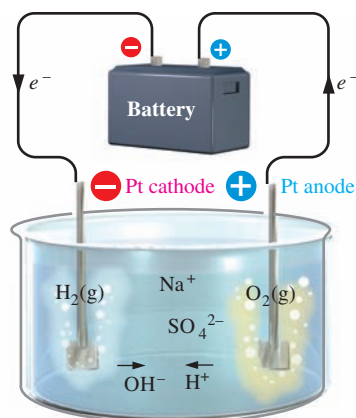


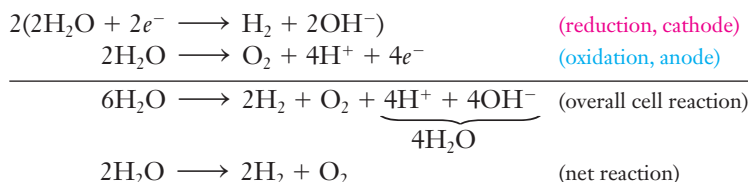
Figure 21-4 The electrolysis of aqueous Na_2SO_4 produces $\text{H}_2(\text{g})$ at the cathode and O_2 at the anode. Bromthymol blue indicator has been added to the solution. This indicator turns blue in the basic solution near the cathode (where OH^- is produced) and yellow in the acidic solution near the anode (where H^+ is formed).

21-5 The Electrolysis of Aqueous Sodium Sulfate

In the electrolysis of aqueous sodium sulfate using inert electrodes, we observe the following.

1. Gaseous H_2 is produced at one electrode. The solution becomes basic around that electrode.
2. Gaseous O_2 is produced at the other electrode. The solution becomes acidic around that electrode.

As in the previous example, water is reduced in preference to Na^+ at the cathode. Observation 2 suggests that water is also preferentially oxidized relative to the sulfate ion, SO_4^{2-} , at the anode (Figure 21-4).



The net result is the electrolysis of water. This occurs because H_2O is both more readily reduced than Na^+ and more readily oxidized than SO_4^{2-} . The ions of Na_2SO_4 conduct the current through the solution, but they take no part in the reaction.

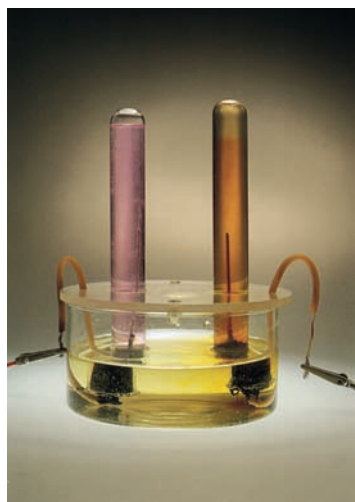
21-6 Counting Electrons: Coulometry and Faraday's Law of Electrolysis

In 1832–1833, Michael Faraday's studies of electrolysis led to this conclusion.

The amount of substance that undergoes oxidation or reduction at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell.



Michael Faraday (1791–1867) is considered the greatest experimental scientist of the 19th century. As a bookbinder's apprentice, he educated himself by extensive reading. Intrigued by his self-study of chemistry and by a lecture given by Sir Humphry Davy, the leading chemist of the day, Faraday applied for a position with Davy at the Royal Institution. He subsequently became director of that laboratory. His public lectures on science were very popular.



The electrolysis of the aqueous solution of KI , another Group 1A–Group 7A salt. At the cathode (left), water is reduced to $\text{H}_2(\text{g})$ and OH^- ions, turning the phenolphthalein indicator pink. The characteristic brownish color of aqueous I_2 appears at the anode (right).



Electrolysis of water to produce $\text{O}_2(\text{g})$ and $\text{H}_2(\text{g})$. Na_2SO_4 was dissolved in the water to improve the conductivity. Can you identify which tube in this picture is collecting the H_2 gas and the name of the electrode producing it (anode or cathode)?

This is **Faraday's Law of Electrolysis**. A quantitative unit of electricity is now called the faraday.

One **faraday** is the amount of electricity that corresponds to the gain or loss, and therefore the passage, of 6.022×10^{23} electrons, or *one mole* of electrons.

A smaller electrical unit commonly used in chemistry, physics, and electronics is the **coulomb (C)**. One coulomb is defined as the amount of charge that passes a given point when 1 ampere (A) of electric current flows for 1 second. One **ampere** of current equals 1 coulomb per second. One faraday is equal to 96,485 coulombs of charge.

- ▶ An ampere is usually called an "amp."
- ▶ For comparison, a 100-watt household incandescent light bulb uses a current of about 0.8 ampere.

$$1 \text{ ampere} = 1 \frac{\text{coulomb}}{\text{second}} \quad \text{or} \quad 1 \text{ A} = 1 \text{ C/s}$$

$$1 \text{ faraday} = 6.022 \times 10^{23} e^- = 96,485 \text{ C}$$

Table 21-1 shows the amounts of several elements produced during electrolysis by the passage of 1 faraday of electricity. The use of electrochemical cells to relate the amount of reactant or product to the amount of current passed is called **coulometry**.

Table 21-1 Amounts of Elements Produced at One Electrode in Electrolysis by 1 Faraday of Electricity

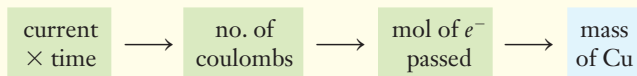
Half-Reaction	Number of e^- in Half-Reaction	Product (electrode)	Amount Produced
$\text{Ag}^+(\text{aq}) + e^- \longrightarrow \text{Ag}(\text{s})$	1	Ag (cathode)	1 mol = 107.868 g
$2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{H}_2(\text{g})$	2	H_2 (cathode)	$\frac{1}{2}$ mol = 1.008 g
$\text{Cu}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Cu}(\text{s})$	2	Cu (cathode)	$\frac{1}{2}$ mol = 31.773 g
$\text{Au}^{3+}(\text{aq}) + 3e^- \longrightarrow \text{Au}(\text{s})$	3	Au (cathode)	$\frac{1}{3}$ mol = 65.656 g
$2\text{Cl}^-(\text{aq}) \longrightarrow \text{Cl}_2(\text{g}) + 2e^-$	2	Cl_2 (anode)	$\frac{1}{2}$ mol = 35.453 g = 11.2 L _{STP}
$2\text{H}_2\text{O}(\ell) \longrightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^-$	4	O_2 (anode)	$\frac{1}{4}$ mol = 8.000 g = 5.60 L _{STP}

EXAMPLE 21-1 Electrolysis

Calculate the mass of copper metal produced at the cathode during the passage of 2.50 amperes of current through a solution of copper(II) sulfate for 50.0 minutes.

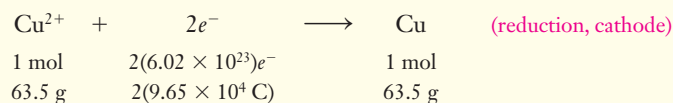
Plan

The half-reaction that describes the reduction of copper(II) ions tells us the number of moles of electrons required to produce one mole of copper metal. Each mole of electrons corresponds to 1 faraday, or 9.65×10^4 coulombs, of charge. The product of current and time gives the number of coulombs.



Solution

The equation for the reduction of copper(II) ions to copper metal is



- ▶ The amount of electricity in Examples 21-1 and 21-2 would be sufficient to light a 100-watt household incandescent light bulb for about 150 minutes, or 2.5 hours.

- ▶ When the number of significant figures in the calculation warrants, the value 96,485 coulombs is usually rounded to 96,500 coulombs ($9.65 \times 10^4 \text{ C}$).

CHEMISTRY IN USE

A Spectacular View of One Mole of Electrons

Early in our study of chemistry, we saw that atoms are made up of protons, neutrons, and electrons. We also discussed the incredibly large size of Avogadro's number, 6.022×10^{23} . Although individual atoms and molecules are invisible to the naked eye, one mole of atoms or molecules is easily detected. Because subatomic particles are even smaller than atoms and also invisible, you might never expect to see individual electrons. Let's consider the possibility, however, of seeing a faraday of charge. A faraday of charge contains Avogadro's number of electrons. Would this collection of 6.022×10^{23} electrons be visible? If so, what might it look like? It would look quite spectacular!

Throughout the 1980s, scientists carefully studied data collected during 5 million lightning flashes along the eastern United States. The data were collected by 36 instruments that were collectively known as the National Lightning Detection Network. The investigating scientists found that the electrical currents in lightning flashes over northern Florida measured about 45,000 amps, about double the 25,000-amp currents in lightning flashes over the New England states. This study showed that the amount of current flowing during lightning flashes was inversely proportional to the latitude (distance from the equator) of the storm.

One coulomb is the amount of charge that passes a point when a one-ampere current flows for one second (1 coulomb = 1 ampere · second). Thus, a current of 96,500 amps flowing for one second contains Avogadro's number of electrons, or one faraday of charge.



Garard/Science Photo Library/Photo Researchers Inc

Measurements taken in northern Florida show that a typical two-second lightning strike over that section of the country would transfer approximately Avogadro's number of electrons between the clouds and the earth. So, for those living in northern Florida, a spectacular mental view of one mole of electrons can be obtained by visualizing a two-second lightning strike. Keep in mind that the average lightning strike lasts only a small fraction of a second, and that we can only have a mental view of a two-second lightning strike by extrapolation of what is seen in nature. Because New England lightning strikes produce only about half the current of lightning strikes over northern Florida, people in New England must try to imagine a four-second lightning strike.

RONALD DELORENZO

STOP & THINK

Remember that $2.50 \text{ A} = 2.50 \text{ C/s}$. Also remember to convert time into seconds when doing these calculations!



Charles D. Winters

A family memento that has been electroplated with copper. To aid in electroplating onto nonconductors, such as shoes, the material is first soaked in a concentrated electrolyte solution to make it conductive.

We see that 63.5 grams of copper “plate out” for every 2 moles of electrons, or for every $2(9.65 \times 10^4 \text{ coulombs})$ of charge. We first calculate the number of coulombs passing through the cell.

$$\underline{\hspace{1cm}} \text{ C} = 50.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{2.50 \text{ C}}{\text{s}} = 7.50 \times 10^3 \text{ C}$$

We calculate the mass of copper produced by the passage of $7.50 \times 10^3 \text{ coulombs}$.

$$\underline{\hspace{1cm}} \text{ g Cu} = 7.50 \times 10^3 \text{ C} \times \frac{1 \text{ mol } e^-}{9.65 \times 10^4 \text{ C}} \times \frac{63.5 \text{ g Cu}}{2 \text{ mol } e^-} = 2.47 \text{ g Cu} \quad (\text{about the mass of a copper penny})$$

Notice how little copper is deposited by this considerable current in 50 minutes.

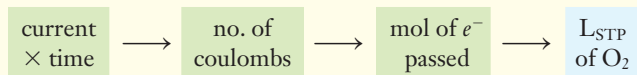
You should now work Exercises 26 and 32.

EXAMPLE 21-2 Electrolysis

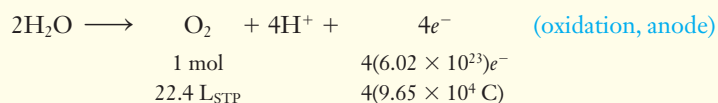
What volume of oxygen gas (measured at STP) is produced by the oxidation of water at the anode in the electrolysis of copper(II) sulfate in Example 21-1?

Plan

We use the same approach as in Example 21-1. Here we relate the amount of charge passed to the number of moles, and hence the volume of O_2 gas produced at STP.

**Solution**

The equation for the oxidation of water and the equivalence between the number of coulombs and the volume of oxygen produced at STP are



The number of coulombs passing through the cell is $7.50 \times 10^3 \text{ C}$. For every $4(9.65 \times 10^4)$ coulombs) passing through the cell, one mole of O_2 (22.4 L at STP) is produced.

$$\begin{aligned}
 \text{? L}_{STP} O_2 &= 7.50 \times 10^3 \text{ C} \times \frac{1 \text{ mol } e^-}{9.65 \times 10^4 \text{ C}} \times \frac{1 \text{ mol } O_2}{4 \text{ mol } e^-} \times \frac{22.4 \text{ L}_{STP} O_2}{1 \text{ mol } O_2} \\
 &= 0.435 \text{ L}_{STP} O_2
 \end{aligned}$$

You should now work Exercise 28.

Notice how little product is formed by what seems to be a lot of electricity. This suggests why electrolytic production of gases and metals is so costly.

21-7 Commercial Applications of Electrolytic Cells

Several elements are produced commercially by electrolysis. In Sections 21-3 to 21-5, we described some electrolytic cells that produce sodium (the Downs cell), chlorine, hydrogen, and oxygen. Electrolysis of molten compounds is also the common method of obtaining other Group 1A metals, 2A metals (except barium), and aluminum (see Section 26-3). Impure metals can also be refined electrolytically, as we will describe for copper in Section 26-8.

Metal-plated articles are common in our society. Jewelry and tableware are often plated with silver. Gold is plated onto jewelry and electrical contacts. Copper is plated onto many objects for decorative purposes (Figure 21-5). Automobiles formerly had steel bumpers plated with thin films of chromium. A chrome bumper required approximately 3 seconds of electroplating to produce a smooth, shiny surface only 0.0002 mm thick. When the metal atoms are deposited too rapidly, they are not able to form extended lattices. Rapid plating of metal results in rough, grainy, black surfaces. Slower plating produces smooth surfaces. “Tin cans” are steel cans plated electrolytically with tin; these are sometimes replaced by cans plated in a fraction of a second with an extremely thin chromium film.



Anodized aluminum is made by oxidizing a piece of aluminum in an electrolytic cell for a short period of time. The oxidation microscopically dissolves some of the Al surface and coats it with a protective and tough coating of aluminum oxide. This creates a matte finish that can be dyed different colors.

Voltaic or Galvanic Cells

Voltaic, or galvanic, cells are electrochemical cells in which *spontaneous* (product-favored) oxidation–reduction reactions produce electrical energy. The two halves of the redox reaction are separated, requiring electron transfer to occur through an external circuit. In

► These cells are named for Allesandro Volta (1745–1827) and Luigi Galvani (1737–1798), two Italian physicists of the 18th century.

Unless otherwise noted, all content on this page is © Cengage Learning.

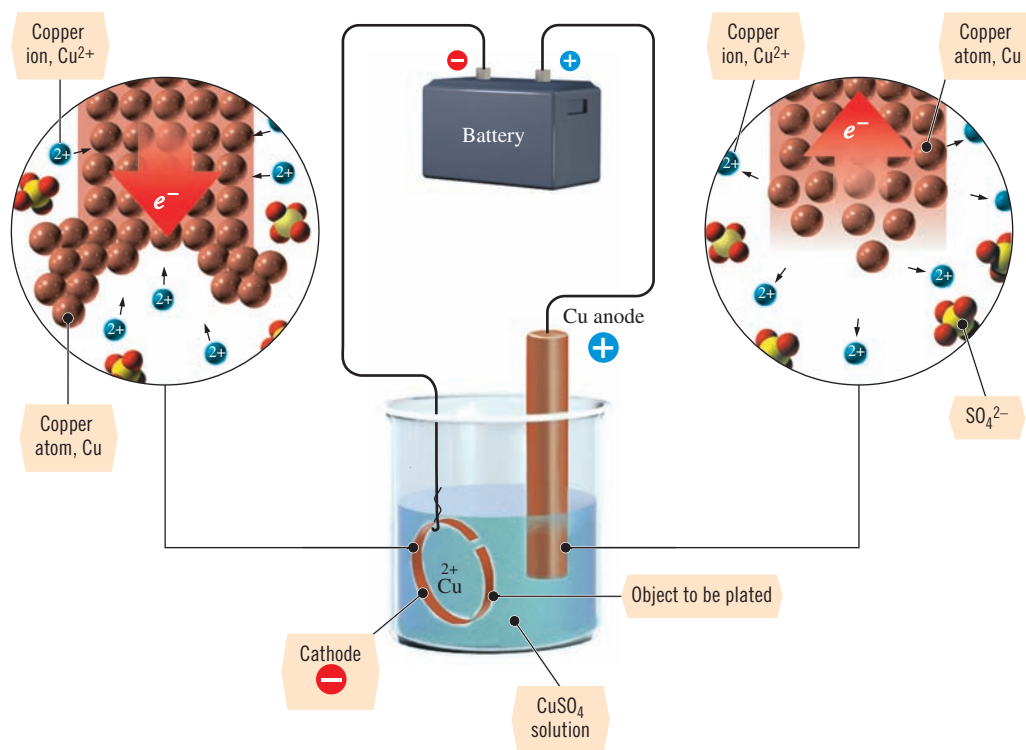


Figure 21-5 Electroplating with copper. The anode is pure copper, which dissolves during the electroplating process. This replenishes the Cu^{2+} ions that are removed from the solution as Cu plates out on the cathode.

this way, useful electrical energy is obtained. Everyone is familiar with some voltaic cells. The batteries commonly used in flashlights, portable radios, photographic equipment, and many toys and appliances are voltaic cells. Automobile batteries consist of voltaic cells connected in series so that their voltages add. We will first consider some simple laboratory cells used to measure the potential difference, or voltage, of a reaction under study. We will then look at some common voltaic cells.

21-8 The Construction of Simple Voltaic Cells

A **half-cell** contains the oxidized and reduced forms of an element, or other more complex species, in contact with one another. A common kind of half-cell consists of a piece of metal (the electrode) immersed in a solution of its ions. Consider two such half-cells in separate beakers (Figure 21-6). The electrodes are connected by a wire. A voltmeter can be inserted into the circuit to measure the potential difference between the two electrodes, or an ammeter can be inserted to measure the current flow. The electric current is the result of the spontaneous redox reaction that occurs. We measure the potential of the cell.

The circuit between the two solutions is completed by a **salt bridge**. This can be any medium through which ions can slowly pass. A salt bridge can be made by bending a piece of glass tubing into the shape of a “U,” filling it with a hot saturated salt/5% agar solution, and allowing it to cool. The cooled mixture “sets” to the consistency of firm gelatin. As a result, the solution does not run out when the tube is inverted (see Figure 21-6), but the ions in the gel are still able to move. A salt bridge serves three functions.

1. It allows electrical contact between the two solutions.
2. It prevents mixing of the electrode solutions.
3. It maintains the electrical neutrality in each half-cell as ions flow into and out of the salt bridge.

► Neither a voltmeter nor an ammeter generates electrical energy. They are designed to measure electrical voltage or the amount of current flow.

► Agar is a porous, gelatinous material obtained from algae.

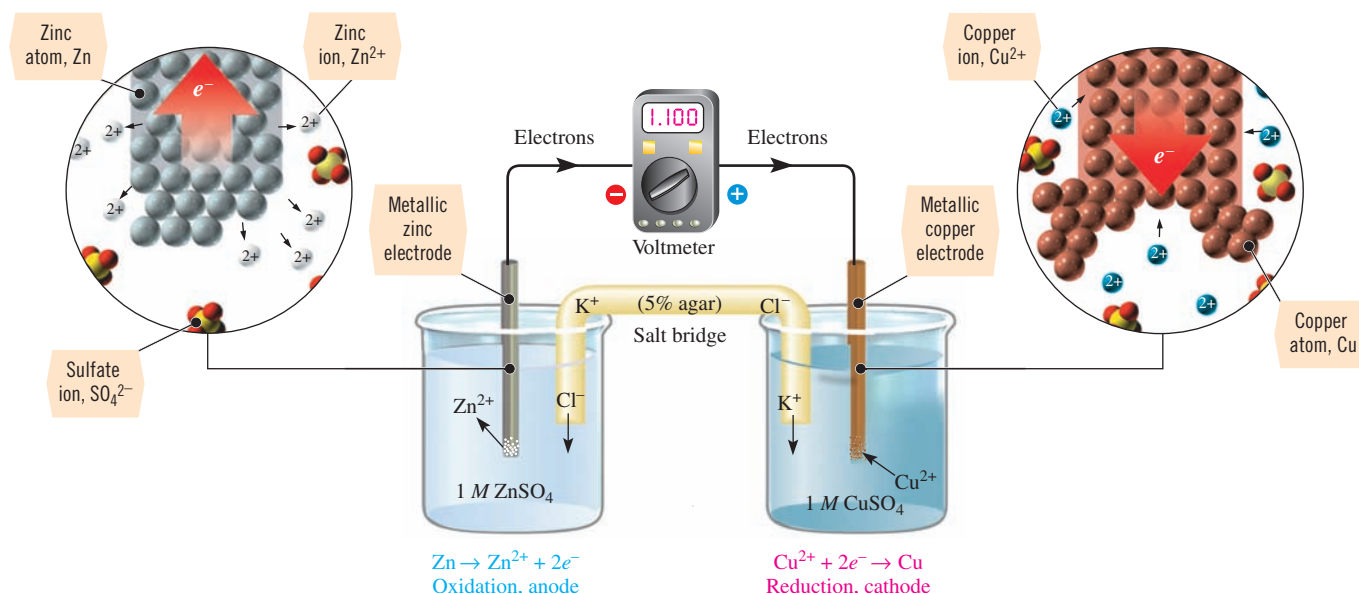


Figure 21-6 The zinc–copper voltaic cell utilizes the reaction



The standard potential of this cell is 1.100 volts.

A cell in which all reactants and products are in their thermodynamic standard states (1 *M* for dissolved species and 1 atm partial pressure for gases) is called a **standard cell**.

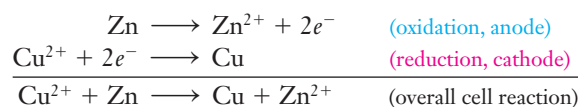
► When we show a concentration in a *standard cell* as 1 *M*, it is assumed to be exactly 1 *M*.

21-9 The Zinc–Copper Cell

Consider a standard cell made up of two half-cells, one a strip of metallic Cu immersed in 1 *M* copper(II) sulfate solution and the other a strip of Zn immersed in 1 *M* zinc sulfate solution (see Figure 21-6). This cell is called the Daniell cell. The following experimental observations have been made about this cell.

1. The initial voltage is 1.100 volts.
2. The mass of the zinc electrode decreases. The concentration of Zn^{2+} *increases* in the solution around the zinc electrode as the cell operates.
3. The mass of the copper electrode increases. The concentration of Cu^{2+} *decreases* in the solution around this electrode as the cell operates.

The Zn electrode loses mass because some Zn metal is *oxidized* to Zn^{2+} ions, which go into solution. Thus the Zn electrode is the *anode*. At the *cathode*, Cu^{2+} ions are *reduced* to Cu metal. This plates out on the electrode, so its mass increases.

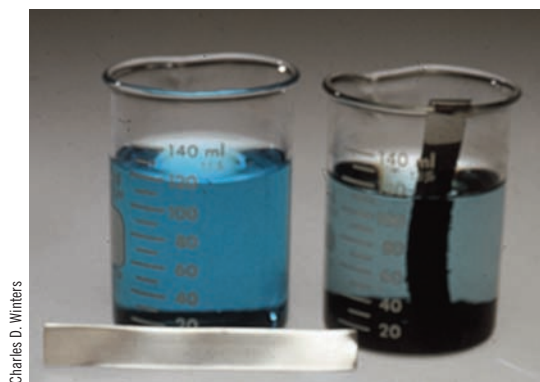


Electrons are released at the anode and consumed at the cathode. They therefore flow through the wire from anode to cathode, as in all electrochemical cells. In all *voltaic* cells, the electrons flow spontaneously from the negative electrode to the positive electrode. So, in contrast with electrolytic cells, the anode is negative and the cathode is positive. To maintain electroneutrality and complete the circuit, two Cl^- ions from the salt bridge migrate into the anode solution for every Zn^{2+} ion formed. Two K^+ ions migrate into the cathode solution to replace every Cu^{2+} ion reduced. Some Zn^{2+} ions from the anode vessel and some SO_4^{2-} ions from the cathode vessel also migrate into the salt bridge. Neither Cl^- nor K^+ ions are oxidized or reduced in preference to the zinc metal or Cu^{2+} ions.

► Reduction, however, still occurs at the cathode (recall the Red Cat) and oxidation at the anode.

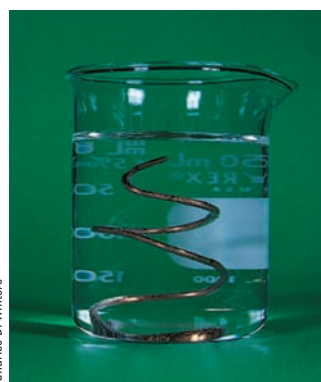
► Compare the $-/+$, anode–cathode, and oxidation–reduction labels and the directions of electron flow in Figures 21-2a and 21-6.

Unless otherwise noted, all content on this page is © Cengage Learning.



Charles D. Winters

A A strip of zinc was placed in a blue solution of copper(II) sulfate, CuSO_4 (left-hand beaker). The Cu^{2+} in solution oxidizes the Zn metal and deposits Cu metal onto the strip of Zn, while the oxidized Zn^{2+} dissolved. The resulting zinc sulfate solution is colorless (right hand beaker). This is the same overall reaction as the one that occurs when the two half-reactions are separated in the zinc–copper cell (Figure 21-6).



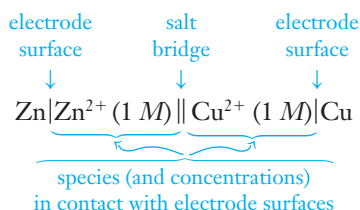
Charles D. Winters

B No reaction occurs when copper wire is placed in a colorless zinc sulfate solution. The reaction $\text{Zn}^{2+} + \text{Cu(s)} \longrightarrow \text{Zn(s)} + \text{Cu}^{2+}$ is the *reverse* of the spontaneous (product-favored) reaction in Figure 21-6, so it is *nonspontaneous* (reactant-favored).

Zn(s)/ $\text{Cu}^{2+}(\text{aq})$ reaction.

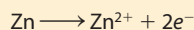
As the redox reaction proceeds consuming the reactants, the cell voltage decreases. When the cell voltage reaches zero, the reaction has reached equilibrium and no further net reaction occurs. At this point, however, the Cu^{2+} ion concentration in the cathode cell is *not* zero. This description applies to any voltaic cell.

Voltaic cells can be represented as follows for the zinc–copper cell.

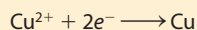


STOP & THINK

This is a shorthand notation for the cell reactions:



and



In this representation, a single line (|) represents an interface at which a potential develops, that is, an electrode. It is conventional to write the anode half-cell on the left in this notation.

The same reaction occurs when a piece of Zn is dropped into a solution of CuSO_4 . The Zn dissolves and the blue color of Cu^{2+} ions disappears. Copper metal forms on the Zn and then settles to the bottom of the container. Because the oxidizing Cu^{2+} ions and reducing Zn metal are in direct contact with one another in this arrangement, the electron transfer is “short-circuited,” so the spontaneous free energy available to perform work is wasted and simply heats the solution. Only by separating the two half-reactions into separate cells and connecting them with an external wire (circuit) and a salt bridge can one effectively use the electricity generated.

Problem-Solving Tip How to Tell the Anode from the Cathode

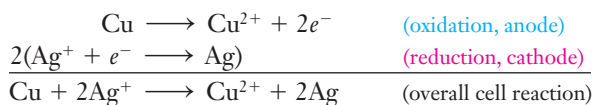
The correspondence between the names *anode* and *cathode* and the charge on the electrode is *different* for electrolytic cells than for voltaic (galvanic) cells. Students sometimes get confused by trying to remember which is which. Check the definitions of these two terms in Section 21-2. The surest way to name these electrodes is to determine what process takes place at each one. Remember the “red cat” mnemonic—*reduction* occurs at the *cathode*, regardless of the type of electrochemical cell one is dealing with.

21-10 The Copper–Silver Cell

Now consider a similar standard voltaic cell consisting of a strip of Cu immersed in 1 M CuSO₄ solution and a strip of Ag immersed in 1 M AgNO₃ solution. A wire and a salt bridge complete the circuit. The following observations have been made.

1. The initial voltage of the cell is 0.462 volt.
2. The mass of the copper electrode decreases. The Cu²⁺ ion concentration *increases* in the solution around the copper electrode.
3. The mass of the silver electrode increases. The Ag⁺ ion concentration *decreases* in the solution around the silver electrode.

In this cell the Cu electrode is the anode because Cu metal is oxidized to Cu²⁺ ions. The Ag electrode is the cathode because Ag⁺ ions are reduced to metallic Ag (Figure 21-7).



As before, ions from the salt bridge migrate to maintain electroneutrality. Some NO₃[−] ions (from the cathode vessel) and some Cu²⁺ ions (from the anode vessel) also migrate into the salt bridge to keep the overall charge balanced. Two NO₃[−] ions migrate for each Cu²⁺ ion.

Recall that in the zinc–copper cell the copper electrode was the *cathode*; now in the copper–silver cell the copper electrode has become the *anode*.

Whether a particular electrode acts as an anode or a cathode in a voltaic cell depends on what the other electrode of the cell is.

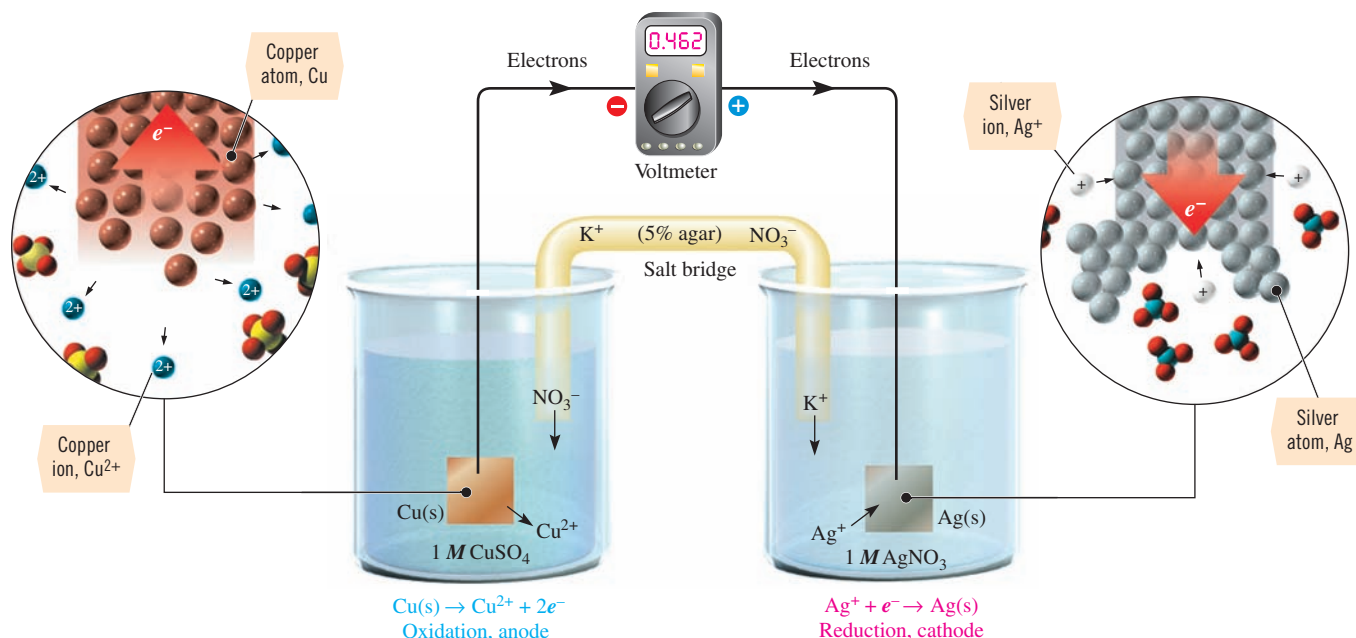


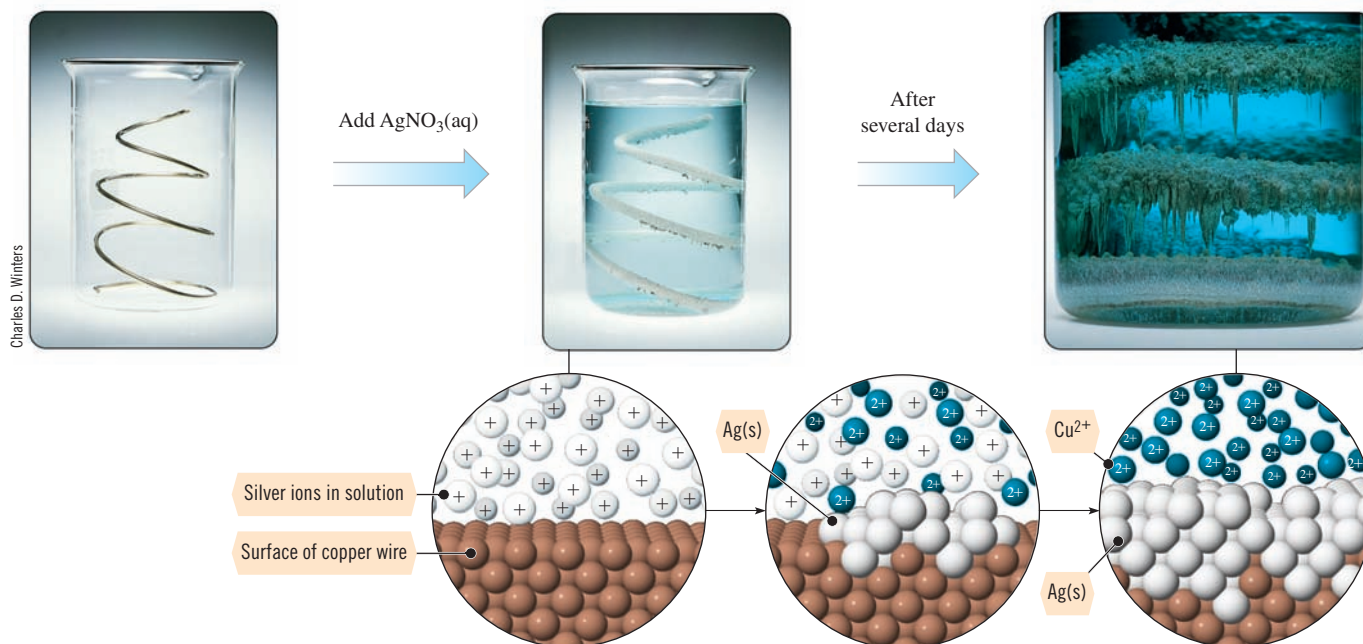
Figure 21-7 The copper–silver voltaic cell utilizes the reaction



The standard potential of this cell is 0.462 volt. This standard cell can be represented as Cu|Cu²⁺ (1 M)||Ag⁺ (1 M)|Ag.

► KCl is not used in this salt bridge because the Cl[−] ions would react with Ag⁺ ions to form insoluble AgCl(s).

Unless otherwise noted, all content on this page is © Cengage Learning.

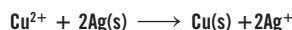


A spiral of copper wire is placed in a colorless solution of silver nitrate, AgNO_3 . The silver is gradually displaced from solution and adheres to the wire. The resulting copper nitrate solution is blue.



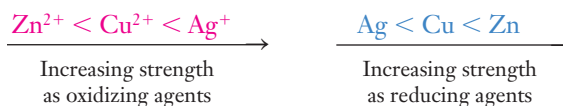
The same spontaneous (product-favored) reaction occurs when the two half-reactions are separated in the copper–silver cell (see Figure 21-7).

No reaction occurs when silver wire is placed in a blue copper sulfate solution. The reaction



is the reverse of the spontaneous reaction shown here and in Figure 21-7; it has a *negative* E_{cell}^0 and is *nonspontaneous* (reactant-favored).

The two cells we have described show that the Cu^{2+} ion is more easily reduced (is a stronger oxidizing agent) than Zn^{2+} , so Cu^{2+} oxidizes metallic zinc to Zn^{2+} . By contrast, the Ag^+ ion is more easily reduced (is a stronger oxidizing agent) than Cu^{2+} , so Ag^+ oxidizes Cu atoms to Cu^{2+} . Conversely, metallic Zn is a stronger reducing agent than metallic Cu, and metallic Cu is a stronger reducing agent than metallic Ag. We can now arrange the species we have studied in order of increasing strength as oxidizing agents and as reducing agents.



Results such as these form the basis for the activity series (see Table 6-9).

Standard Electrode Potentials

The potentials of the standard zinc–copper and copper–silver voltaic cells are 1.100 volts and 0.462 volt, respectively. The magnitude of a cell's potential measures the spontaneity of its redox reaction. *Higher (more positive) cell potentials indicate greater driving force for the reaction as written.* Under standard conditions, the oxidation of metallic Zn by Cu^{2+} ions has a greater tendency to go toward completion than does the oxidation of metallic Cu by Ag^+ ions. It is convenient to separate the total cell potential into the individual contributions of the two half-reactions. This lets us determine the relative tendencies of particular oxidation or reduction half-reactions to occur. Such information gives us a quantitative

basis for specifying strengths of oxidizing and reducing agents. In the next several sections, we shall see how this is done for standard half-cells.

21-11 The Standard Hydrogen Electrode

Every oxidation must be accompanied by a reduction (i.e., the electrons must have somewhere to go). So it is impossible to determine experimentally the potential of any *single* electrode. We therefore establish an arbitrary standard. The conventional reference electrode is the **standard hydrogen electrode (SHE)**. This electrode contains a piece of metal electrolytically coated with a grainy black surface of inert platinum metal (finely divided metals such as Pt often appear black), immersed in a 1 M H⁺ solution. Hydrogen, H₂, is bubbled at 1 atm pressure through a glass envelope over the platinized electrode (Figure 21-8).

By international convention, the standard hydrogen electrode is arbitrarily assigned a potential of *exactly* 0.0000 . . . volt.

SHE Half-Reaction	E^0 (standard electrode potential)	
$\text{H}_2 \longrightarrow 2\text{H}^+ + 2e^-$	exactly 0.0000 . . . V	(SHE as anode)
$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	exactly 0.0000 . . . V	(SHE as cathode)

As we shall see in Section 21-14, this arbitrary definition will provide a basis on which to describe the relative potential (and hence the relative spontaneity) of any half-cell process. We can construct a standard cell consisting of a standard hydrogen electrode and some other standard electrode (half-cell). Because the defined electrode potential of the SHE contributes exactly 0 volts to the sum, the voltage of the overall cell is then attributed entirely to the other half-cell.

21-12 The Zinc–SHE Cell

This cell consists of a SHE in one beaker and a strip of zinc immersed in 1 M zinc chloride solution in another beaker (Figure 21-9). A wire and a salt bridge complete the circuit. When the circuit is closed, the following observations can be made.

1. The initial potential of the cell is 0.763 volt.
2. As the cell operates, the mass of the zinc electrode decreases. The concentration of Zn²⁺ ions increases in the solution around the zinc electrode.
3. The H⁺ concentration decreases in the SHE. Gaseous H₂ is produced.

We can conclude from these observations that the following half-reactions and cell reaction occur.

		E^0	
(oxidation, anode)	$\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$	0.763 V	
(reduction, cathode)	$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	0.000 V	(by definition)
(cell reaction)	$\text{Zn} + 2\text{H}^+ \longrightarrow \text{Zn}^{2+} + \text{H}_2$	$E^0_{\text{cell}} = 0.763 \text{ V}$	(measured)

The standard potential at the anode *plus* the standard potential at the cathode gives the standard cell potential. The potential of the SHE is 0.000 volts, and the standard cell potential is found to be 0.763 volt. So the standard potential of the zinc anode in this cell must be 0.763 volt. The Zn|Zn²⁺(1.0 M)||H⁺(1.0 M), H₂(1 atm)|Pt cell is depicted in Figure 21-9.

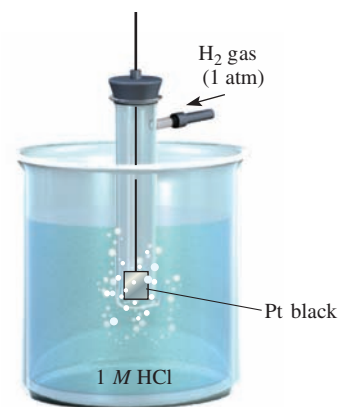


Figure 21-8 The standard hydrogen electrode (SHE). A molecular-level view of the operation of the SHE as a cathode is shown in Figure 21-9 and as an anode in Figure 21-10.

► The superscript in E^0 indicates thermodynamic standard-state conditions.

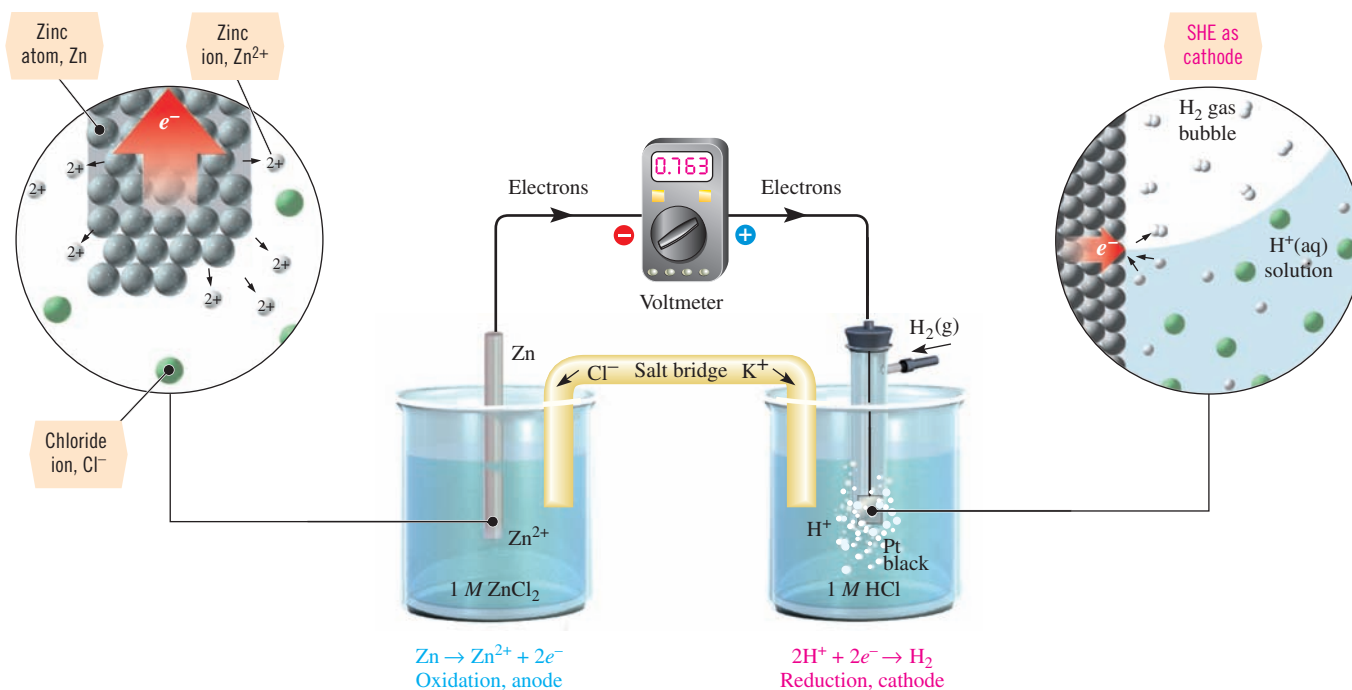
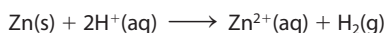


Figure 21-9 The $\text{Zn}|\text{Zn}^{2+}(1\text{ M})||\text{H}^+(1\text{ M}); \text{H}_2(1\text{ atm})|\text{Pt}$ cell, in which the following net reaction occurs.



In this cell, the standard hydrogen electrode functions as the cathode.

Note that in *this* cell, H^+ is reduced to H_2 , so the SHE is the *cathode*. At the other electrode, metallic zinc is oxidized to Zn^{2+} , so the zinc electrode is the *anode* in this cell.

The idea of “electron pressure” helps us to understand this process. The positive potential for the half-reaction



says that this oxidation is *more favorable* than the corresponding oxidation of H_2 ,



Before they are connected, each half-cell builds up a supply of electrons waiting to be released, thus generating an electron pressure. The process with the more *positive* E^0 value is favored, so we reason that the electron pressure generated at the Zn electrode is greater than that at the H_2 electrode. As a result, when the cell is connected, the electrons released by the oxidation of Zn flow through the wire *from the Zn electrode to the H_2 electrode*, where they are consumed by the reduction of H^+ ions. Oxidation occurs at the zinc electrode (anode), and reduction occurs at the hydrogen electrode (cathode).

► What we have informally called “electron pressure” is the tendency to undergo oxidation.

21-13 The Copper–SHE Cell

Another voltaic cell consists of a SHE in one beaker and a strip of Cu metal immersed in 1 M copper(II) sulfate solution in another beaker. A wire and a salt bridge complete the circuit. For this cell, we observe the following (Figure 21-10).

1. The initial cell potential is 0.337 volt.
2. Gaseous hydrogen is consumed. The H^+ concentration *increases* in the solution of the SHE.
3. The mass of the copper electrode increases. The concentration of Cu^{2+} ions *decreases* in the solution around the copper electrode.

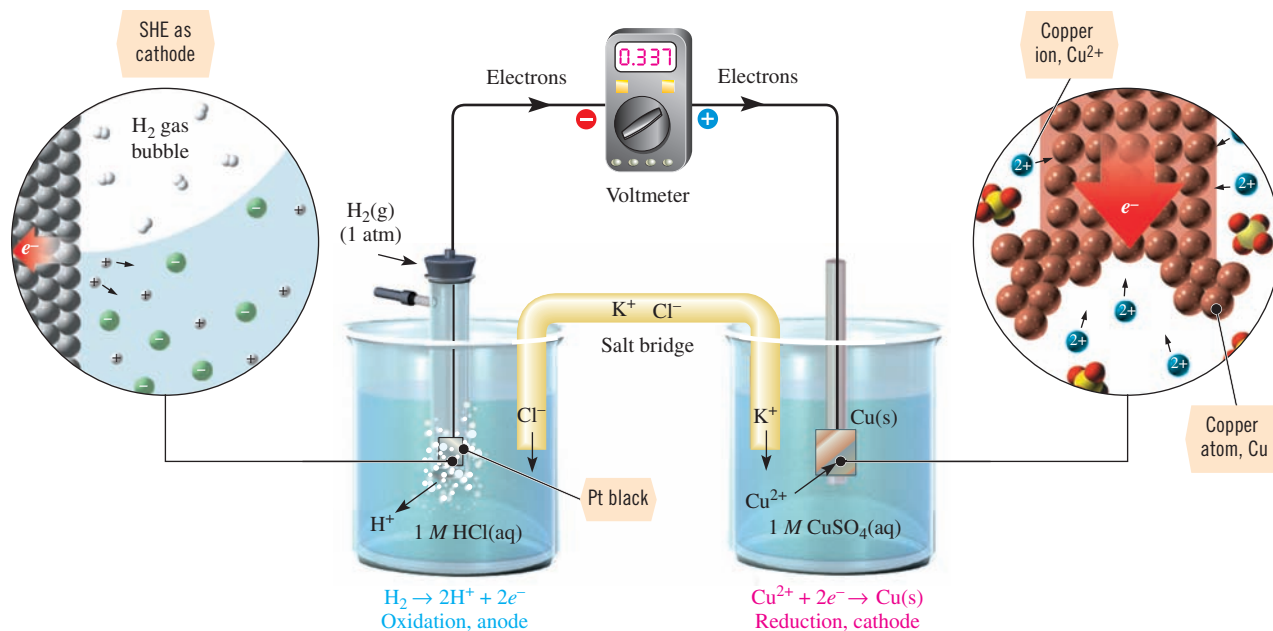
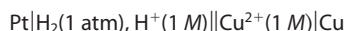


Figure 21-10 The standard copper-SHE cell,



In this cell, the standard hydrogen electrode functions as the anode. The net reaction is



Thus, the following half-reactions and cell reaction occur.

		E^0	
(oxidation, anode)	$\text{H}_2 \longrightarrow 2\text{H}^+ + 2e^-$	0.000 V	(by definition)
(reduction, cathode)	$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	0.337 V	
(cell reaction)	$\text{H}_2 + \text{Cu}^{2+} \longrightarrow 2\text{H}^+ + \text{Cu}$	$E^0_{\text{cell}} = 0.337 \text{ V}$	(measured)

The SHE functions as the *anode* in this cell, and Cu²⁺ ions oxidize H₂ to H⁺ ions. The standard electrode potential of the copper half-cell is 0.337 volt as a *cathode* in the Cu-SHE cell.

Again, we can think of $E^0_{\text{oxidation}}$ in the two half-cells as “electron pressures.”



Now we see that the hydrogen electrode has the higher electron pressure (more positive, less negative E^0_{oxid}). When the cell is connected, electrons flow through the wire from the hydrogen electrode to the copper electrode. H₂ is oxidized to 2H⁺ (anode), and Cu²⁺ is reduced to Cu (cathode).

► Recall that in the Zn-SHE cell the SHE was the *cathode*.

► When we reverse the Cu half-reaction to write it as an oxidation, we must reverse its sign.

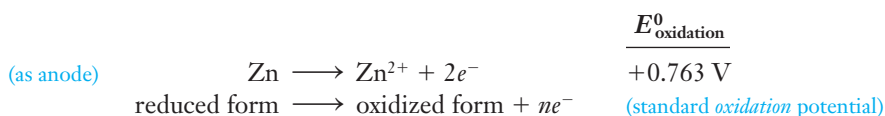
21-14 Standard Electrode Potentials

We can develop a series of representative electrode potentials by measuring the potentials of other standard electrodes versus the SHE in the way we have described for the standard Zn-SHE and standard Cu-SHE voltaic cells. The **standard electrode potential** for any half-cell is its potential with respect to the standard hydrogen electrode, measured at 25°C when the concentration of each ion in the solution is 1 M and the pressure of any gas involved is 1 atm.

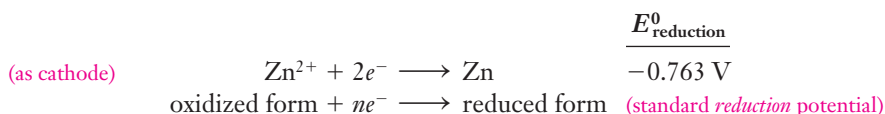
► The activity series (see Table 6-9) is based on standard electrode potentials.

By convention, we always tabulate the standard electrode potential for each half-cell as a *reduction* process.

Many electrodes involve metals or nonmetals in contact with their ions. We saw (Section 21-12) that the standard Zn electrode behaves as the anode versus the SHE and that the standard *oxidation* potential for the Zn half-cell is 0.763 volt.



The *reduction* potential for the standard zinc electrode (to act as a *cathode* relative to the SHE) is therefore the negative of this, or -0.763 volt.



By international convention, the standard potentials of electrodes are tabulated for *reduction half-reactions*. These indicate the tendencies of the electrodes to behave as cathodes toward the SHE. Electrodes with positive E^0 values for reduction half-reactions act as cathodes versus the SHE. Those with negative E^0 values for reduction half-reactions act as anodes versus the SHE.

Electrodes with <i>Positive</i> $E^0_{\text{reduction}}$	Electrodes with <i>Negative</i> $E^0_{\text{reduction}}$
Reduction occurs <i>more readily</i> than the reduction of 2H^{+} to H_2 .	Reduction is <i>more difficult</i> than the reduction of 2H^{+} to H_2 .
Electrode acts as a <i>cathode</i> versus the SHE (which acts as the anode).	Electrode acts as an <i>anode</i> versus the SHE (which acts as the cathode).

The more positive the E^0 value for a half-reaction, the greater the tendency for the half-reaction to occur in the forward direction as written. Conversely, the more negative the E^0 value for a half-reaction, the greater the tendency for the half-reaction to occur in the reverse direction as written.

Table 21-2 lists standard reduction potentials for a few elements.

► The oxidizing agent is reduced.

1. The species on the *left* side are all cations of metals, hydrogen ions, or elemental nonmetals. These are all *oxidizing agents* (*oxidized forms* of the elements). Their strengths as oxidizing agents increase from top to bottom, that is, as the $E^0_{\text{reduction}}$ values become more positive. Fluorine, F_2 , is the strongest oxidizing agent, and Li^{+} is a very weak oxidizing agent.

► The reducing agent is oxidized.

2. The species on the *right* side are free metals, hydrogen, or anions of nonmetals. These are all *reducing agents* (*reduced forms* of the elements). Their strengths as reducing agents increase from bottom to top, that is, as the $E^0_{\text{reduction}}$ values become more negative. Metallic Li is a very strong reducing agent, and F^{-} is a very weak reducing agent.

The more positive the reduction potential, the stronger the species on the left is as an oxidizing agent and the weaker the species on the right is as a reducing agent.

Table 21-2 Standard Reduction Potentials in Aqueous Solution at 25°C

Element	Reduction Half-Reaction		Standard Reduction Potential E^0 (volts)
Li	$\text{Li}^+ + e^-$	$\longrightarrow \text{Li}$	-3.045
K	$\text{K}^+ + e^-$	$\longrightarrow \text{K}$	-2.925
Ca	$\text{Ca}^{2+} + 2e^-$	$\longrightarrow \text{Ca}$	-2.87
Na	$\text{Na}^+ + e^-$	$\longrightarrow \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2e^-$	$\longrightarrow \text{Mg}$	-2.37
Al	$\text{Al}^{3+} + 3e^-$	$\longrightarrow \text{Al}$	-1.66
Zn	$\text{Zn}^{2+} + 2e^-$	$\longrightarrow \text{Zn}$	-0.763
Cr	$\text{Cr}^{3+} + 3e^-$	$\longrightarrow \text{Cr}$	-0.74
Fe	$\text{Fe}^{2+} + 2e^-$	$\longrightarrow \text{Fe}$	-0.44
Cd	$\text{Cd}^{2+} + 2e^-$	$\longrightarrow \text{Cd}$	-0.403
Ni	$\text{Ni}^{2+} + 2e^-$	$\longrightarrow \text{Ni}$	-0.25
Sn	$\text{Sn}^{2+} + 2e^-$	$\longrightarrow \text{Sn}$	-0.14
Pb	$\text{Pb}^{2+} + 2e^-$	$\longrightarrow \text{Pb}$	-0.126
H_2	$2\text{H}^+ + 2e^-$	$\longrightarrow \text{H}_2$	0.000 (reference electrode)
Cu	$\text{Cu}^{2+} + 2e^-$	$\longrightarrow \text{Cu}$	+0.337
I_2	$\text{I}_2 + 2e^-$	$\longrightarrow 2\text{I}^-$	+0.535
Hg	$\text{Hg}^{2+} + 2e^-$	$\longrightarrow \text{Hg}$	+0.789
Ag	$\text{Ag}^+ + e^-$	$\longrightarrow \text{Ag}$	+0.799
Br_2	$\text{Br}_2 + 2e^-$	$\longrightarrow 2\text{Br}^-$	+1.08
Cl_2	$\text{Cl}_2 + 2e^-$	$\longrightarrow 2\text{Cl}^-$	+1.360
Au	$\text{Au}^{3+} + 3e^-$	$\longrightarrow \text{Au}$	+1.50
F_2	$\text{F}_2 + 2e^-$	$\longrightarrow 2\text{F}^-$	+2.87

21-15 Uses of Standard Electrode Potentials

The most important application of electrode potentials is the prediction of the spontaneity of redox reactions. Standard electrode potentials can be used to determine the spontaneity of redox reactions in general, whether or not the reactions can take place in electrochemical cells.

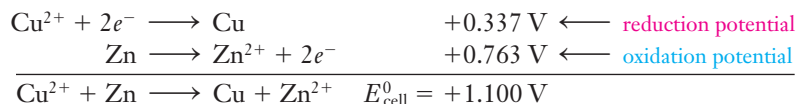
Suppose we ask the question: At standard conditions, will Cu^{2+} ions oxidize metallic Zn to Zn^{2+} ions, or will Zn^{2+} ions oxidize metallic copper to Cu^{2+} ? One of the two possible reactions is spontaneous, and the reverse reaction is nonspontaneous. We must determine which one is spontaneous. We already know the answer to this question from experimental results (see Section 21-9), but let us demonstrate the procedure for predicting the spontaneous reaction from known values of standard electrode potentials.

1. Choose the appropriate half-reactions from a table of standard reduction potentials.
2. Write the equation for the half-reaction with the more positive (or less negative) E^0 value *for reduction*, along with its potential.
3. Write the equation for the other half-reaction *as an oxidation* and write its *oxidation potential*; to do this, reverse the tabulated reduction half-reaction and change the sign of E^0 . (Reversing a half-reaction or a complete reaction also changes the sign of its potential.)
4. Balance the electron transfer. *We do not multiply the potentials by the numbers used to balance the electron transfer!* The reason is that each potential represents a *tendency* for a reaction process to occur relative to the SHE; this does not depend on *how many times* it occurs. An electric potential is an *intensive property*.

Unless otherwise noted, all content on this page is © Cengage Learning.

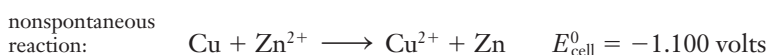
5. Add the reduction and oxidation half-reactions, and add the reduction and oxidation potentials. E_{cell}^0 will be *positive* for the resulting overall cell reaction. This indicates that the reaction as written is *product-favored (spontaneous)*. A *negative* E_{cell}^0 value would indicate that the reaction is *reactant-favored (nonspontaneous)*.

For the cell described here, the Cu^{2+}/Cu couple has the more positive reduction potential, so we keep it as the reduction half-reaction and reverse the other half-reaction. Following the steps outlined, we obtain the equation for the spontaneous (product-favored) reaction.



The positive E_{cell}^0 value tells us that the forward reaction is spontaneous (product-favored) at standard conditions. So we conclude that copper(II) ions oxidize metallic zinc to Zn^{2+} ions as they are reduced to metallic copper. (Section 21-9 shows that the potential of the standard zinc-copper voltaic cell is 1.100 volts. This is the spontaneous reaction that occurs.)

The reverse reaction has a negative E^0 and is nonspontaneous.



To make it occur, we would have to supply electrical energy with a potential difference greater than 1.100 volts. That is, this nonspontaneous reaction would have to be carried out in an *electrolytic cell*.

EXAMPLE 21-3 Predicting the Direction of Reactions

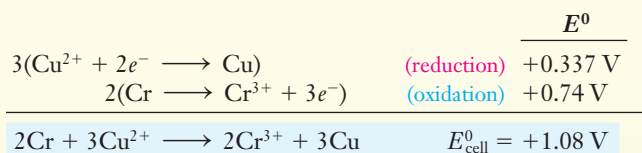
At standard conditions, will chromium(III) ions, Cr^{3+} , oxidize metallic copper to copper(II) ions, Cu^{2+} , or will Cu^{2+} oxidize metallic chromium to Cr^{3+} ions? Write the equation for the spontaneous (product-favored) reaction and calculate E_{cell}^0 for this reaction.

Plan

We refer to the table of standard reduction potentials (see Appendix J) and choose the two appropriate half-reactions.

Solution

The copper half-reaction has the more positive reduction potential, so we write it first. Then we write the chromium half-reaction as an oxidation, balance the electron transfer, and add the two half-reactions and their potentials.



Because E_{cell}^0 is positive, we know that the reaction is spontaneous (product-favored).

Cu^{2+} ions spontaneously oxidize metallic Cr to Cr^{3+} ions and are reduced to metallic Cu.

You should now work Exercise 58a.

STOP & THINK

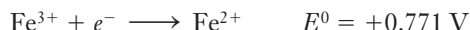
It is very important to change the sign of the E^0 potential whenever you reverse a half-reaction, as with the chromium equation shown here. But remember that we do *not* multiply the E^0 potentials by the factors used to balance the number of electrons when we add the half-reactions together to give the overall balanced equation.

Problem-Solving Tip The Sign of E^0 Indicates Spontaneity

For a reaction that is spontaneous at *standard conditions*, E_{cell}^0 must be positive. A negative value of E_{cell}^0 indicates that the reverse of the reaction written would be spontaneous at standard conditions.

21-16 Standard Electrode Potentials for Other Half-Reactions

In some half-cells, the oxidized and reduced species are both in solution as ions in contact with inert electrodes. For example, the standard iron(III) ion/iron(II) ion half-cell contains 1 *M* concentrations of the two ions. It involves the following half-reaction.



The standard dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ion/chromium(III) ion half-cell consists of a 1 *M* concentration of each of the two ions in contact with an inert electrode. The balanced half-reaction in acidic solution (1.0 *M* H^{+}) is



Standard reduction potentials for some other reactions are given in Table 21-3 and in Appendix J. These potentials can be used like those of Table 21-2.

► Platinum metal is often used as the inert electrode material. These two standard half-cells could be shown in shorthand notation as $\text{Pt}|\text{Fe}^{3+}(1 \text{ M}), \text{Fe}^{2+}(1 \text{ M})$ and $\text{Pt}|\text{Cr}_2\text{O}_7^{2-}(1 \text{ M}), \text{Cr}^{3+}(1 \text{ M})$

STOP & THINK

If H^{+} appears anywhere in the half-reaction, the solution is acidic. The presence of OH^{-} means that the solution is basic.

Table 21-3 Standard Reduction Potentials for Selected Half-Cells

Reduction Half-Reaction		Standard Reduction Potential E° (volts)
$\text{Zn}(\text{OH})_4^{2-} + 2e^{-}$	$\longrightarrow \text{Zn} + 4\text{OH}^{-}$	−1.22
$\text{Fe}(\text{OH})_2 + 2e^{-}$	$\longrightarrow \text{Fe} + 2\text{OH}^{-}$	−0.877
$2\text{H}_2\text{O} + 2e^{-}$	$\longrightarrow \text{H}_2 + 2\text{OH}^{-}$	−0.828
$\text{PbSO}_4 + 2e^{-}$	$\longrightarrow \text{Pb} + \text{SO}_4^{2-}$	−0.356
$\text{NO}_3^{-} + \text{H}_2\text{O} + 2e^{-}$	$\longrightarrow \text{NO}_2^{-} + 2\text{OH}^{-}$	+0.01
$\text{Sn}^{4+} + 2e^{-}$	$\longrightarrow \text{Sn}^{2+}$	+0.15
$\text{AgCl} + e^{-}$	$\longrightarrow \text{Ag} + \text{Cl}^{-}$	+0.222
$\text{Hg}_2\text{Cl}_2 + 2e^{-}$	$\longrightarrow 2\text{Hg} + 2\text{Cl}^{-}$	+0.27
$\text{O}_2 + 2\text{H}_2\text{O} + 4e^{-}$	$\longrightarrow 4\text{OH}^{-}$	+0.40
$\text{NiO}_2 + 2\text{H}_2\text{O} + 2e^{-}$	$\longrightarrow \text{Ni}(\text{OH})_2 + 2\text{OH}^{-}$	+0.49
$\text{H}_3\text{AsO}_4 + 2\text{H}^{+} + 2e^{-}$	$\longrightarrow \text{H}_3\text{AsO}_3 + \text{H}_2\text{O}$	+0.58
$\text{Fe}^{3+} + e^{-}$	$\longrightarrow \text{Fe}^{2+}$	+0.771
$\text{ClO}^{-} + \text{H}_2\text{O} + 2e^{-}$	$\longrightarrow \text{Cl}^{-} + 2\text{OH}^{-}$	+0.89
$\text{NO}_3^{-} + 4\text{H}^{+} + 3e^{-}$	$\longrightarrow \text{NO} + 2\text{H}_2\text{O}$	+0.96
$\text{O}_2 + 4\text{H}^{+} + 4e^{-}$	$\longrightarrow 2\text{H}_2\text{O}$	+1.229
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^{+} + 6e^{-}$	$\longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33
$\text{Cl}_2 + 2e^{-}$	$\longrightarrow 2\text{Cl}^{-}$	+1.360
$\text{MnO}_4^{-} + 8\text{H}^{+} + 5e^{-}$	$\longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.507
$\text{PbO}_2 + \text{HSO}_4^{2-} + 3\text{H}^{+} + 2e^{-}$	$\longrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	+1.685

EXAMPLE 21-4 Predicting the Direction of Reactions

In an acidic solution at standard conditions, will tin(IV) ions, Sn^{4+} , oxidize gaseous nitrogen oxide, NO , to nitrate ions, NO_3^{-} , or will NO_3^{-} oxidize Sn^{2+} to Sn^{4+} ions? Write the equation for the spontaneous (product-favored) reaction and calculate E_{cell}° for this reaction.

Plan

We refer to the table of standard reduction potentials (Table 21-3) and choose the appropriate half-reactions.

STOP & THINK

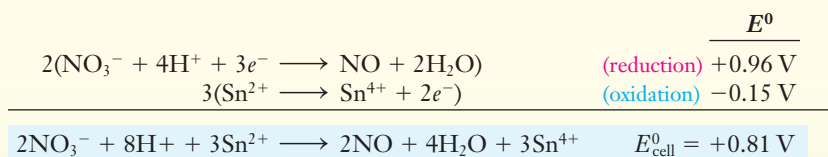
Pay careful attention to the conditions (acidic or basic) and the half-cell reactions mentioned in the problem. For example, there also is a half-reaction in Table 21-3 with NO_3^{-} being reduced to NO_2^{-} in basic solution. This is not the correct half-reaction to use for this question.

STOP & THINK

Remember the italicized warning in Step 4 of the procedure set out in Section 21-15. *We do not multiply the potentials by the numbers used to balance the electron transfer!* Doing so is a very common error in E°_{cell} calculations.

Solution

The NO_3^-/NO reduction half-reaction has the more positive E° value, so we write it first and write the $\text{Sn}^{4+}/\text{Sn}^{2+}$ half-reaction as an oxidation. We balance the electron transfer and add the two half-reactions to obtain the equation for the *spontaneous* reaction. Then we add the half-reaction potentials to obtain the overall cell potential.



Because E°_{cell} is positive for this reaction,

nitrate ions spontaneously oxidize tin(II) ions to tin(IV) ions and are reduced to nitrogen oxide in acidic solution.

You should now work Exercises 59 and 60.

► Remember that temperature is not officially part of standard conditions. But most thermodynamic data are given at a temperature of 25°C.

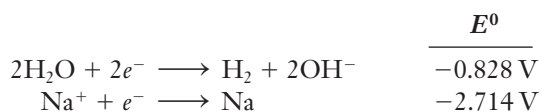
Problem-Solving Tip Remember What We Mean by Standard Conditions

When we say that a reaction takes place at *standard conditions*, we mean the following:

1. The temperature is the standard thermodynamic temperature, 25°C, unless stated otherwise.
2. All reactants and products are at *unit activity*. This means that
 - a. Any solution species that takes part in the reaction is at a concentration of exactly 1 M;
 - b. Any gas that takes part in the reaction is at a pressure of exactly 1 atm;
 - c. Any other substance that takes part in the reaction is *pure*.

(When we say “takes part in the reaction,” we mean either as a reactant or a product.) These are the same conditions that were described as *standard state conditions* for thermodynamic purposes (see Section 15-6). When one or more of these conditions is not satisfied, we must adjust our calculations for nonstandard conditions. We shall learn how to do this in Section 21-19.

Now that we know how to use standard reduction potentials, let's see how they explain the reaction that occurs in the electrolysis of aqueous NaCl. The first two electrolytic cells we considered involved *molten* NaCl and *aqueous* NaCl (see Sections 21-3 and 21-4). There was no doubt that in molten NaCl, metallic Na would be produced by reduction of Na^+ , and gaseous Cl_2 would be produced by oxidation of Cl^- . But we found in aqueous NaCl that H_2O , rather than Na^+ , was reduced. This is consistent with the less negative reduction potential of H_2O compared with Na^+ .



The more easily reduced species, H_2O , is reduced.

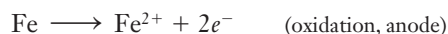
Electrode potentials measure only the relative *thermodynamic* likelihood for various half-reactions. In practice, kinetic factors can complicate matters. For instance, sometimes the electrode process is limited by the rate of diffusion of dissolved species to or from the electrode surface. At some cathodes, the rate of electron transfer from the electrode to a reactant is the rate-limiting step, and a higher voltage (called *overvoltage*) must be applied to accom-

plish the reduction. As a result of such factors, a half-reaction that is *thermodynamically* more favorable than some other process still might not occur at a significant rate. In the electrolysis of NaCl(aq), Cl^- is oxidized to Cl_2 gas (-1.360 V), instead of H_2O being oxidized to form O_2 gas (-1.229 V), because of the overvoltage of O_2 on Pt, the inert electrode.

21-17 Corrosion

Ordinary **corrosion** is the redox process by which metals are oxidized by oxygen, O_2 , in the presence of moisture. There are other kinds, but this is the most common. The problem of corrosion and its prevention are of both theoretical and practical interest. Corrosion is responsible for the loss of billions of dollars annually in metal products. The mechanism of corrosion has been studied extensively. It is now known that the oxidation of metals occurs most readily at points of strain (where the metals are most “active”). Thus, a steel nail, which is mostly iron (see Section 26-7), first corrodes at the tip and head (Figure 21-11). A bent nail corrodes most readily at the bend.

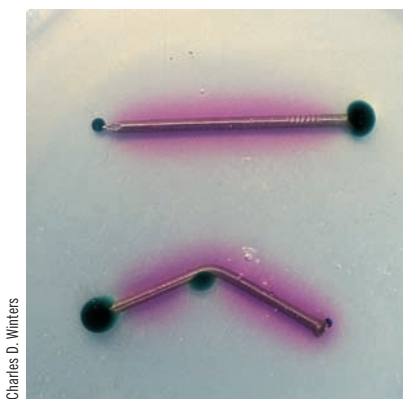
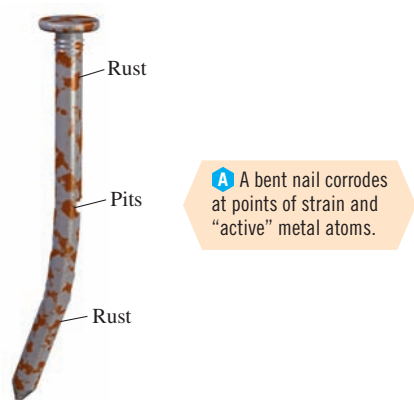
A point of strain in a steel object acts as an anode where the iron is oxidized to iron(II) ions, and pits are formed (Figure 21-12).



The electrons produced then flow through the nail to areas exposed to O_2 . These act as cathodes where oxygen is reduced to hydroxide ions, OH^- .



► Salt (NaCl) does not, in itself, do any active corrosion. It merely accelerates the corrosion of most metals, especially steel, by making the water layer more electrically conductive. This makes it easier for O_2 to oxidize the metal, via the electrically conducting saltwater, without having to diffuse through the water layer to come into physical contact with the metal surface.



► Two nails were placed in an agar gel that contained phenolphthalein and potassium ferricyanide, $\text{K}_3[\text{Fe}(\text{CN})_6]$. As the nails corrode, they produce Fe^{2+} ions at each end and at the bend (an oxidation, so these are anodic regions). Fe^{2+} ions react with $[\text{Fe}(\text{CN})_6]^{3-}$ ions to form $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$, an intensely blue-colored compound. The rest of each nail functions as the cathode, at which water is reduced to H_2 and OH^- ions. The OH^- ions turn phenolphthalein pink.

Figure 21-11 Corrosion of steel (iron).

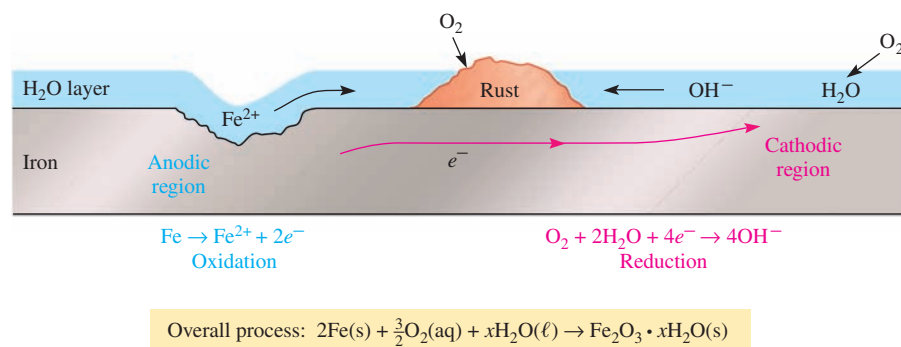
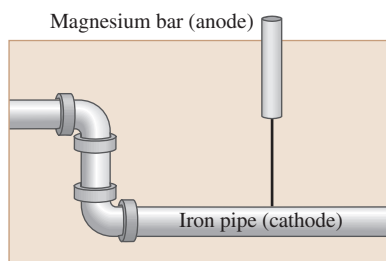


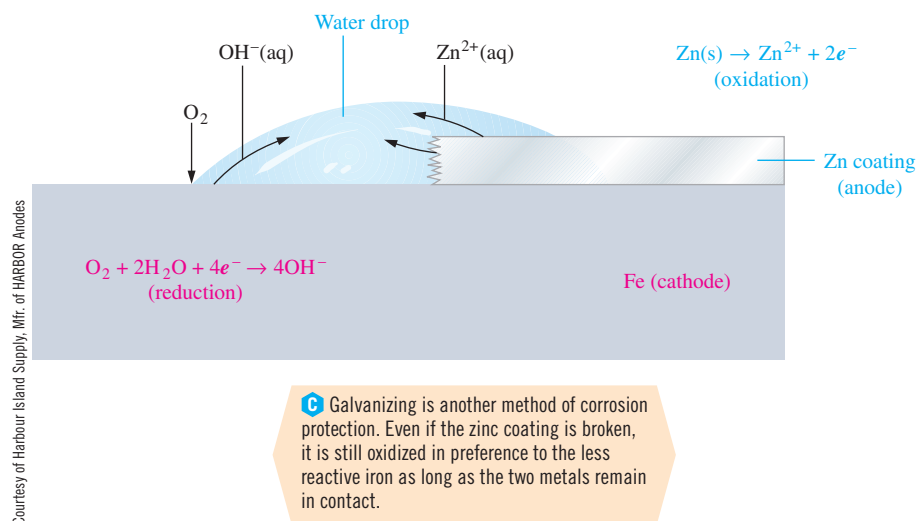
Figure 21-12 The corrosion of iron. Pitting appears at the anodic region, where iron metal is initially oxidized to Fe^{2+} and then to Fe^{3+} . Rust appears at the cathodic region.



A Cathodic protection of buried iron pipe. A magnesium or zinc bar is oxidized instead of the iron. The “sacrificial” anode eventually must be replaced.

B Cathodic protection of a ship's hull. The small yellow horizontal strips are blocks of titanium (coated with platinum) that are attached to the ship's hull. The hull is steel (mostly iron). When the ship is in salt water, the titanium blocks become the anode, and the hull the cathode, in a voltaic cell. Because oxidation always occurs at the anode, the ship's hull (the cathode) is protected from oxidation (corrosion).

Courtesy of Harbour Island Supply, Mfr. of HARBOR Anodes



C Galvanizing is another method of corrosion protection. Even if the zinc coating is broken, it is still oxidized in preference to the less reactive iron as long as the two metals remain in contact.

Figure 21-13 Various methods to protect metal objects from corrosion.



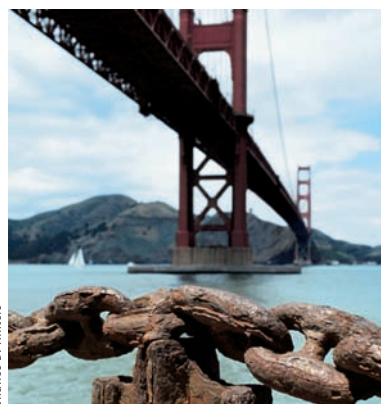
Charles D. Winters

Galvanized objects are made of steel that is coated with zinc to protect against corrosion.



Photodisc/Getty Images

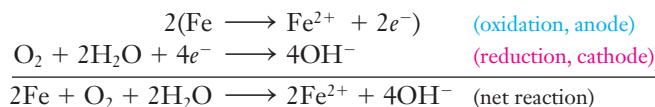
Steel is plated with chromium for appearance as well as protection against corrosion.



Charles D. Winters

Corrosion is an undesirable electrochemical reaction with very serious economic consequences.

At the same time, the Fe^{2+} ions migrate through the moisture on the surface. The overall reaction is obtained by balancing the electron transfer and adding the two half-reactions.



The Fe^{2+} ions can migrate from the anode through the solution toward the cathode region, where they combine with OH^- ions to form iron(II) hydroxide. Iron is further oxidized by O_2 to the +3 oxidation state. The material we call rust is a complex hydrated form of iron(III) oxides and hydroxides with variable water composition; it can be represented as $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. The overall reaction for the rusting of iron is



► Note that water is needed for O_2 to oxidize iron. Dry O_2 will not, therefore, oxidize iron to form rust, nor does water without any O_2 have any ability to oxidize iron.

21-18 Corrosion Protection

There are several methods for protecting metals against corrosion. The most widely used are

1. Plating the metal with a thin layer of a less easily oxidized metal
2. Connecting the metal directly to a **sacrificial anode**, a piece of another metal that is more active and therefore is preferentially oxidized
3. Allowing a protective film, such as a metal oxide, to form naturally on the surface of the metal
4. Galvanizing, or coating steel with zinc, a more active metal
5. Applying a protective coating, such as paint

The thin layer of tin on tin-plated steel cans is less easily oxidized than iron, and it protects the steel underneath from corrosion. It is deposited either by dipping the can into molten tin or by electroplating. Copper is also less active than iron (see Table 21-2). It is sometimes deposited by electroplating to protect metals when food is not involved. Whenever the layer of tin or copper is breached, the iron beneath it corrodes even more rapidly than it would without the coating because of the adverse electrochemical cell that is set up.

Figure 21-13a shows an iron pipe connected to a strip of magnesium, a more active metal, to protect the iron from oxidation. The magnesium is preferentially oxidized. It is called a “sacrificial anode.” Similar methods are used to protect bridges and the hulls of ships from corrosion. Other inexpensive active metals, such as zinc, are also used as sacrificial anodes. Galvanizing (coating the iron with zinc) combines these two approaches. Even if the zinc coating is broken so the iron is exposed, the iron is not oxidized as long as it is in contact with the more easily oxidized zinc (see Figure 21-13c).

Aluminum, a very active metal, reacts rapidly with O_2 from the air to form a surface layer of aluminum oxide, Al_2O_3 , so thin that it is transparent. This very tough, hard substance is inert to oxygen, water, and most other corrosive agents in the environment. In this way, objects made of aluminum form their own protective layers and need not be treated further to inhibit corrosion. Iron oxide, unfortunately, does not form a protective coating on iron or steel. Instead it expands and flakes off, exposing fresh iron for further corrosion.

► Compare the potentials for the reduction half-reactions to see which metal is more easily oxidized. The more positive the reduction potential for a metal, the more stable the metal is as the free element and the harder it is to oxidize.

	$E^\circ_{\text{reduction}}$
$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	−2.37 V
$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	−0.763 V
$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	−0.44 V
$\text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}$	−0.14 V
$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	+0.337 V

► Acid rain endangers structural aluminum by dissolving this Al_2O_3 coating.

Effect of Concentrations (or Partial Pressures) on Electrode Potentials

21-19 The Nernst Equation

Standard electrode potentials, designated E° , refer to standard-state conditions. These standard-state conditions are one molar solutions for ions and one atmosphere pressure for gases with all solids and liquids in their standard states at 25°C. As any of the standard

STOP & THINK
Remember that we refer to *thermodynamic* standard-state conditions and not standard temperature and pressure as in gas law calculations.

Unless otherwise noted, all content on this page is © Cengage Learning.

cells described earlier operates, and concentrations or pressures of reactants change, the observed cell voltage drops. Similarly, cells constructed with solution concentrations different from one molar, or gas pressures different from one atmosphere, cause the corresponding potentials to deviate from standard electrode potentials.

The **Nernst equation** is used to calculate electrode potentials and cell potentials for concentrations and partial pressures other than standard-state values.

► In this equation, the expression following the minus sign represents how much the *nonstandard* conditions cause the electrode potential to deviate from its standard value, E^0 . The Nernst equation is normally presented in terms of base-10 logarithms, as we will do in this text.

$$E = E^0 - \frac{2.303 RT}{nF} \log Q$$

where

E = potential under the *nonstandard* conditions

E^0 = *standard* potential

R = gas constant, $8.314 \text{ J/mol} \cdot \text{K}$

T = absolute temperature in K

n = number of moles of electrons transferred in the reaction or half-reaction

F = faraday, $96,485 \text{ C/mol } e^- \times 1 \text{ J/(V} \cdot \text{C)} = 96,485 \text{ J/V} \cdot \text{mol } e^-$

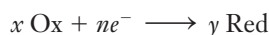
Q = reaction quotient

The reaction quotient, Q , was introduced in Section 17-4. It involves a ratio of concentrations or pressures of products to those of reactants, each raised to the power indicated by the coefficient in the balanced equation. The Q expression used in the Nernst equation is the thermodynamic reaction quotient; it can include *both* concentrations and pressures. Substituting these values into the Nernst equation at 25°C gives

► At 25°C , the value of $\frac{2.303 RT}{F}$ is 0.0592; at any other temperature, this term must be recalculated. Can you show that this term has the units $\text{V} \cdot \text{mol}$?

$$E = E^0 - \frac{0.0592}{n} \log Q \quad (\text{Note: in terms of base-10 log})$$

In general, half-reactions for standard reduction potentials are written



“Ox” refers to the oxidized species and “Red” to the reduced species; x and y are their coefficients, respectively, in the balanced equation. The Nernst equation for any *cathode* half-cell (*reduction* half-reaction) is

$$E = E^0 - \frac{0.0592}{n} \log \frac{[\text{Red}]^y}{[\text{Ox}]^x} \quad (\text{for reduction half-reaction})$$

For the familiar half-reaction involving metallic zinc and zinc ions,



the corresponding Nernst equation is

$$E = E^0 - \frac{0.0592}{2} \log \frac{1}{[\text{Zn}^{2+}]} \quad (\text{for reduction})$$

► Metallic Zn is a pure solid, so its concentration does not appear in Q .

We substitute the E^0 value into the equation to obtain

$$E = -0.763 \text{ V} - \frac{0.0592}{2} \log \frac{1}{[\text{Zn}^{2+}]}$$

EXAMPLE 21-5 The Nernst Equation for a Half-Cell Reaction

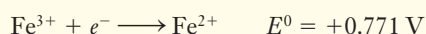
Calculate the potential, E , for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ electrode when the concentration of Fe^{2+} is exactly five times that of Fe^{3+} .

Plan

The Nernst equation lets us calculate potentials for concentrations other than one molar. The tabulation of standard reduction potentials gives us the value of E^0 for the reduction half-reaction. We use the balanced half-reaction and the given concentration ratio to calculate the value of Q . Then we substitute this into the Nernst equation, with n equal to the number of moles of electrons involved in the half-reaction.

Solution

The reduction half-reaction is



We are told that the concentration of Fe^{2+} is five times that of Fe^{3+} , or $[\text{Fe}^{2+}] = 5[\text{Fe}^{3+}]$. Calculating the value of Q ,

$$Q = \frac{[\text{Red}]^y}{[\text{Ox}]^x} = \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = \frac{5[\text{Fe}^{3+}]}{[\text{Fe}^{3+}]} = 5$$

The balanced half-reaction shows one mole of electrons, or $n = 1$. Putting values into the Nernst equation,

$$\begin{aligned} E &= E^0 - \frac{0.0592}{n} \log Q = +0.771 - \frac{0.0592}{1} \log 5 = (+0.771 - 0.041) \text{ V} \\ &= +0.730 \text{ V} \end{aligned}$$

You should now work Exercise 82.

► The potential for this electrode is lower than E^0 for the standard $\text{Fe}^{3+}/\text{Fe}^{2+}$ electrode, in which both concentrations are 1 M . This should make qualitative sense to you from having studied LeChatelier's Principle. The more products that are present relative to reactants, the less the driving force (lower potential) to make more products.

The Nernst equation can be applied to balanced equations for redox reactions. One approach is to correct the reduction potential for each half-reaction to take into account the nonstandard concentrations or pressures.

EXAMPLE 21-6 The Nernst Equation for an Overall Cell Reaction

A cell is constructed at 25°C as follows. One half-cell consists of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in which $[\text{Fe}^{3+}] = 1.00 \text{ M}$ and $[\text{Fe}^{2+}] = 0.100 \text{ M}$; the other involves the $\text{MnO}_4^-/\text{Mn}^{2+}$ couple in acidic solution in which $[\text{MnO}_4^-] = 1.00 \times 10^{-2} \text{ M}$, $[\text{Mn}^{2+}] = 1.00 \times 10^{-4} \text{ M}$, and $[\text{H}^+] = 1.00 \times 10^{-3} \text{ M}$. (a) Find the electrode potential for each half-cell with these concentrations, and (b) calculate the overall cell potential.

Plan

(a) We can apply the Nernst equation to find the reduction potential of each half-cell with the stated concentrations. (b) As in Section 21-15, we write the half-reaction with the more positive potential (*after* correction) along with its potential. We reverse the other half-reaction and change the sign of its E value. We balance the electron transfer and then add the half-reactions and their nonstandard, corrected potentials to find the overall cell potential.

Solution(a) For the $\text{MnO}_4^-/\text{Mn}^{2+}$ half-cell as a reduction,

$$\begin{aligned}
 \text{MnO}_4^- + 8\text{H}^+ + 5e^- &\longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} & E^0 &= +1.507 \text{ V} \\
 E &= E^0 - \frac{0.0592}{n} \log \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8} \\
 &= +1.507 \text{ V} - \frac{0.0592}{5} \log \frac{1.00 \times 10^{-4}}{(1.00 \times 10^{-2})(1.00 \times 10^{-3})^8} \\
 &= +1.507 \text{ V} - \frac{0.0592}{5} \log (1.00 \times 10^{22}) = +1.507 \text{ V} - \frac{0.0592}{5} (22.0) \\
 &= +1.246 \text{ V}
 \end{aligned}$$

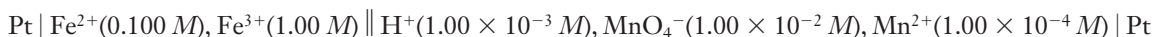
(b) For the $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell as a reduction,

$$\begin{aligned}
 \text{Fe}^{3+} + e^- &\longrightarrow \text{Fe}^{2+} & E^0 &= +0.771 \text{ V} \\
 E &= E^0 - \frac{0.0592}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = +0.771 \text{ V} - \frac{0.0592}{1} \log \frac{0.100}{1.00} \\
 &= +0.771 \text{ V} - \frac{0.0592}{1} \log (0.100) = +0.771 \text{ V} - \frac{0.0592}{1} (-1.00) \\
 &= +0.830 \text{ V}
 \end{aligned}$$

The corrected potential for the $\text{MnO}_4^-/\text{Mn}^{2+}$ half-cell is greater than that for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ half-cell, so we reverse the latter, balance the electron transfer, and add.

	<u><i>E</i> (corrected)</u>
$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.246 V
$5(\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-)$	-0.830 V
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$	$E_{\text{cell}} = 0.416 \text{ V}$

The cell in Example 21-6 can be represented in shorthand notation as



The reaction as written is spontaneous (product-favored) under the stated conditions, with a potential of +0.416 volt *when the cell starts operation*. As the cell discharges and current flows, the product concentrations, $[\text{Mn}^{2+}]$ and $[\text{Fe}^{3+}]$, increase. At the same time, reactant concentrations, $[\text{MnO}_4^-]$, $[\text{H}^+]$, and $[\text{Fe}^{2+}]$, decrease. This increases the magnitude of $\log Q_{\text{cell}}$, so the correction factor becomes more negative. Thus, the overall E_{cell} *decreases* (the reaction becomes less favorable). Eventually the cell potential approaches zero (equilibrium), and the cell “runs down.” The cell is completely run down ($E_{\text{cell}} = 0$) when the term $\frac{0.0592}{n} \log Q_{\text{cell}}$ is equal in magnitude to E_{cell}^0 .

We can also find the cell potential for a nonstandard cell by first finding E_{cell}^0 for the overall standard cell reaction, and then using the Nernst equation to correct for nonstandard concentrations. The next example illustrates this approach.

EXAMPLE 21-7 The Nernst Equation for an Overall Cell Reaction

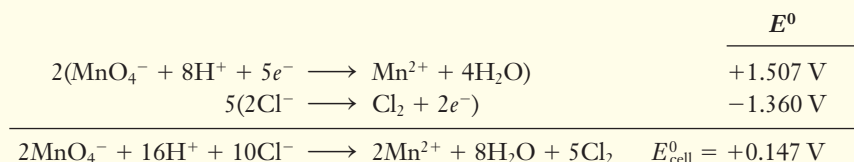
A cell is constructed at 25°C as follows. One half-cell consists of a chlorine/chloride, Cl_2/Cl^- , electrode with the partial pressure of $\text{Cl}_2 = 0.100 \text{ atm}$ and $[\text{Cl}^-] = 0.100 \text{ M}$. The other half-cell involves the $\text{MnO}_4^-/\text{Mn}^{2+}$ couple in acidic solution with $[\text{MnO}_4^-] = 0.100 \text{ M}$, $[\text{Mn}^{2+}] = 0.100 \text{ M}$, and $[\text{H}^+] = 0.100 \text{ M}$. Apply the Nernst equation to the overall cell reaction to determine the cell potential for this cell.

Plan

First we determine the overall cell reaction and its *standard* cell potential, E_{cell}^0 , as in Examples 21-3 and 21-4. Then we apply the Nernst equation to the overall cell.

Solution

The $\text{MnO}_4^-/\text{Mn}^{2+}$ half-reaction has the more positive reduction potential, so we write it first. Then we write the Cl_2/Cl^- half-reaction as an oxidation, balance the electron transfer, and add the two half-reactions and their potentials to obtain the overall cell reaction and its E_{cell}^0 .



In the overall reaction, $n = 10$. We then apply the Nernst equation to this overall reaction by substituting appropriate concentration and partial pressure values. Because Cl_2 is a gaseous component, its term in the Nernst equation involves its partial pressure, P_{Cl_2} , in atm.

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^0 - \frac{0.0592}{n} \log \frac{[\text{Mn}^{2+}]^2 (P_{\text{Cl}_2})^5}{[\text{MnO}_4^-]^2 [\text{H}^+]^{16} [\text{Cl}^-]^{10}} \\
 &= 0.147 \text{ V} - \frac{0.0592}{10} \log \frac{(0.100)^2 (0.100)^5}{(0.100)^2 (0.100)^{16} (0.100)^{10}} \\
 &= 0.147 \text{ V} - \frac{0.0592}{10} \log (1.00 \times 10^{21}) \\
 &= 0.147 \text{ V} - \frac{0.0592}{10} (21.00) = 0.023 \text{ V}
 \end{aligned}$$

You should now work Exercises 84 and 90.

► Can you write the shorthand notation for this cell?

► When evaluating Q in the Nernst equation, remember that (a) molar concentrations are used for dissolved species, and (b) partial pressures of gases are expressed in atmospheres. Units are omitted.

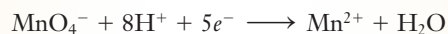
The method illustrated in Example 21-7, applying the Nernst equation to the *overall* cell reaction, usually involves less calculation than correcting the separate half-reactions as in Example 21-6. We interpret our results as follows: The positive overall cell potentials in Examples 21-6 and 21-7 tell us that each of these cell reactions is spontaneous *in the direction written* for the concentrations given. If the resulting cell potential were negative, the *reverse* reaction would be favored at those concentrations. We could then reverse the equation for the overall cell reaction and change the sign of its potential to describe the spontaneous operation of the cell.

► Now solve Example 21-6 by applying the Nernst equation to the *overall* cell reaction to determine the cell potential.

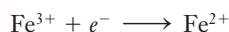
Problem-Solving Tip Be Careful of the Value of n

How do you know what value of n to use? Remember that n must be the number of moles of electrons transferred in the *balanced* equation for the process to which you apply the Nernst equation.

1. For a *half-reaction*, n represents the number of moles of electrons in that half-reaction. In Example 21-6 we applied the Nernst equation to each half-reaction separately, so we used $n = 5$ for the half-reaction



and we used $n = 1$ for the half-reaction



2. For an *overall reaction*, n represents the total number of moles of electrons transferred. In Example 21-7 we applied the Nernst equation to an *overall* reaction in which 10 moles of electrons was transferred from 10 moles of Cl^- to 2 moles of MnO_4^- , so we used the value $n = 10$.

21-20 Using Electrochemical Cells to Determine Concentrations

In Section 21-19, we used known concentrations to predict cell voltage. We can reverse this reasoning and apply the same ideas to *measure* the voltage of a cell and then use the Nernst equation to solve for an *unknown* concentration. The following example illustrates such an application.

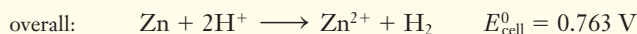
► This cell is similar to the zinc–hydrogen cell that we discussed in Section 21-12, except that the hydrogen concentration is not (necessarily) 1.00 M.

EXAMPLE 21-8 The Nernst Equation

We construct an electrochemical cell at 25°C as follows. One half-cell is a standard Zn^{2+}/Zn cell, that is, a strip of zinc immersed in a 1.00 M Zn^{2+} solution; the other is a *nonstandard* hydrogen electrode in which a platinum electrode is immersed in a solution of *unknown* hydrogen ion concentration with gaseous hydrogen bubbling through it at a pressure of 1.000 atm. The observed cell voltage is 0.522 V. (a) Calculate the value of the reaction quotient Q . (b) Calculate $[\text{H}^+]$ in the second half-cell. (c) Determine the pH of the solution in the second half-cell.

Plan

We saw in Section 21-12 that the zinc–hydrogen cell operated with oxidation at the zinc electrode and reduction at the hydrogen electrode, with a *standard* cell potential of 0.763 V.



(a) We rearrange the Nernst equation to solve for the reaction quotient, Q , from the measured cell voltage with $n = 2$. (b) We substitute concentrations and partial pressures in the expression for Q . Then we can solve for the only unknown, $[\text{H}^+]$. (c) The pH can be determined from the $[\text{H}^+]$ determined in Part (b).

Solution

$$(a) \quad E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0592}{n} \log Q$$

Substituting and solving for Q ,

$$\begin{aligned} 0.522 \text{ V} &= 0.763 \text{ V} - \frac{0.0592}{2} \log Q \\ \frac{0.0592}{2} \log Q &= (0.763 - 0.522) \text{ V} = 0.241 \text{ V} \end{aligned}$$

$$\log Q = \frac{(2)(0.241 \text{ V})}{0.0592 \text{ V}} = 8.14$$

$$Q = 10^{8.14} = 1.4 \times 10^8$$

(b) We write the expression for Q from the balanced overall equation, and solve for $[\text{H}^+]$.

$$\begin{aligned} Q &= \frac{[\text{Zn}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2} \\ [\text{H}^+]^2 &= \frac{[\text{Zn}^{2+}]P_{\text{H}_2}}{Q} = \frac{(1.00)(1.00)}{1.4 \times 10^8} = 7.1 \times 10^{-9} \end{aligned}$$

$$[\text{H}^+] = 8.4 \times 10^{-5} \text{ M}$$

$$(c) \quad \text{pH} = -\log [\text{H}^+] = -\log (8.4 \times 10^{-5}) = 4.08$$

You should now work Exercises 85 and 86.



Courtesy of Lazar Research Laboratories Inc

Microelectrodes have been developed to measure concentrations in very small volumes of solution.

Unless otherwise noted, all content on this page is © Cengage Learning.

A **pH meter** contains a voltaic cell, such as that in Example 21-8, that can be used to measure the $[\text{H}^+]$ concentration and thus the pH of an unknown solution. It is inconvenient to bubble hydrogen gas at a controlled pressure through a hydrogen electrode, so the routine use of this electrode in many environments is not practical. A typical commercial pH meter (Figure 21-14) incorporates a miniaturized pair of electrodes that are more portable and less fragile. One of these electrodes is a **glass electrode**, usually consisting of an AgCl-coated silver wire in contact with an HCl solution of known concentration (usually 1.00 M) in a thin-walled glass bulb (see Figure 21-14a). A **saturated calomel electrode** is often used as the second half-cell (reference electrode). This consists of a platinum wire in contact with a paste of liquid mercury and solid mercury(I) chloride, $\text{Hg}_2\text{Cl}_2(\text{s})$, all immersed in a saturated solution of potassium chloride, KCl. When the glass electrode is placed in a solution, a potential is developed across the thin glass membrane; this potential depends on the $[\text{H}^+]$ concentration, and hence on the pH. The overall voltage of this cell thus measures the pH of the solution in contact with the glass electrode. Each change of one pH unit causes a voltage change of 0.0592 volts. The pH meter is designed to measure very small voltages, and its display is calibrated to give a direct readout of the pH of the solution. Meters of this general design have many routine but important applications in medicine, chemistry, biology, agriculture, environmental analysis, and numerous other areas. Glass electrodes can be made small enough to be implanted into blood vessels or even individual living cells.

Electrochemical procedures that use the principles illustrated here provide a convenient method for making many concentration measurements.

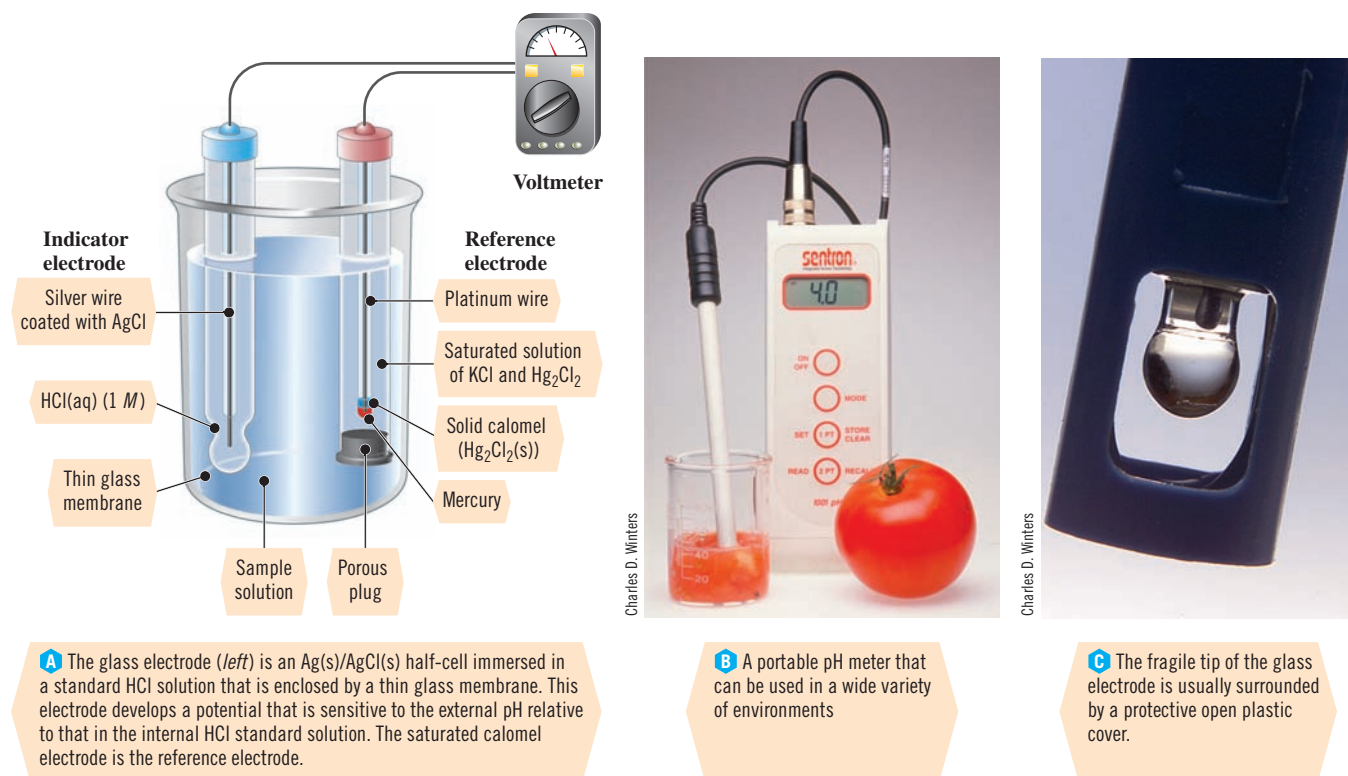


Figure 21-14 The workings of a commercial pH meter.

Unless otherwise noted, all content on this page is © Cengage Learning.

ENRICHMENT

Concentration Cells

As we have seen, different concentrations of ions in a half-cell result in different half-cell potentials. We can use this idea to construct a **concentration cell**, in which both half-cells are composed of the same species but in different ion concentrations. Suppose we set up such a cell using the Cu^{2+}/Cu half-cell that we introduced in Section 21-9. We put copper electrodes into two aqueous solutions, one that is 0.10 M CuSO_4 and another that is 1.00 M CuSO_4 . To complete the cell construction, we connect the two electrodes with a wire and join the two solutions with a salt bridge as usual (Figure 21-15). Now the relevant standard reduction half-reaction in either half-cell is



Thus the Cu^{2+} ions in the more concentrated half-cell can be considered as the reactant, and those in the more dilute cell as the product.



The overall cell potential can be calculated by applying the Nernst equation to the overall cell reaction. We must first find E^0 , the standard cell potential *at standard concentrations*; because the same electrode and the same type of ions are involved in both half-cells, this E^0_{cell} is always zero. Thus,

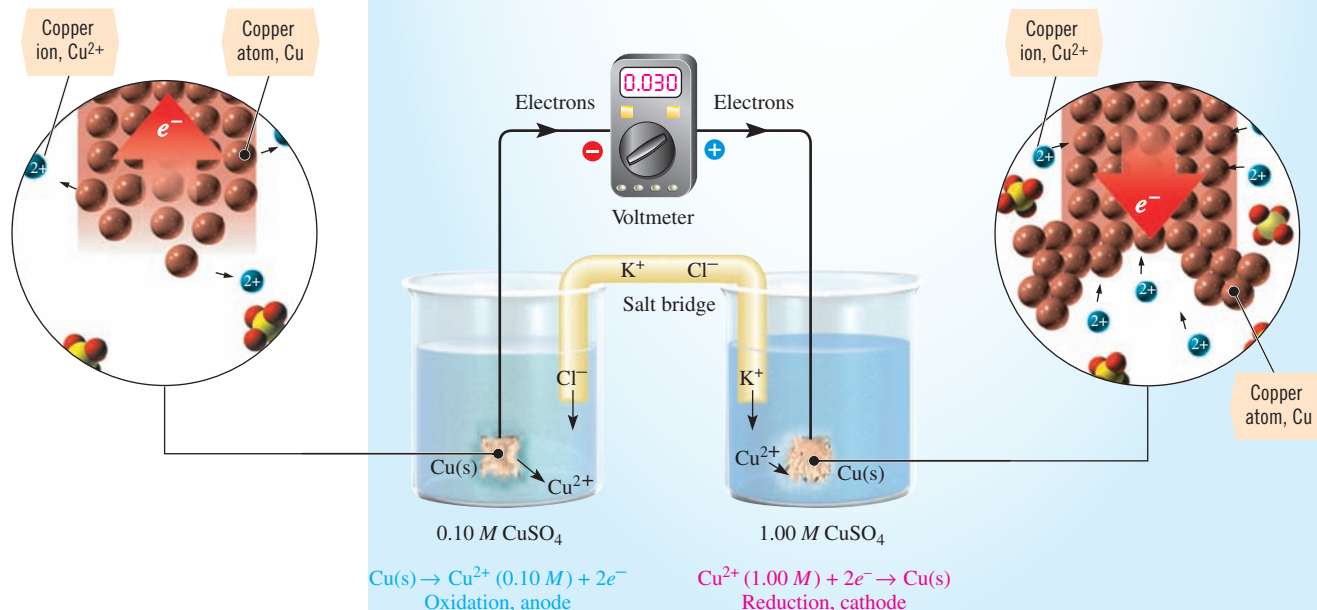
$$\begin{aligned} E_{\text{cell}} &= E^0_{\text{cell}} - \frac{0.0592}{n} \log \frac{[\text{dilute solution}]}{[\text{concentrated solution}]} \\ &= 0 - \frac{0.0592}{2} \log \frac{0.10}{1.00} = +0.030\text{ V} \end{aligned}$$

► The overall cell potential is positive; the reaction is spontaneous as written.

Figure 21-15 The concentration cell $\text{Cu}|\text{Cu}^{2+}(0.10\text{ M})||\text{Cu}^{2+}(1.00\text{ M})|\text{Cu}$. The overall reaction lowers the $[\text{Cu}^{2+}]$ concentration in the more concentrated solution and increases it in the more dilute solution.

As the reaction proceeds, $[\text{Cu}^{2+}]$ decreases in the more concentrated half-cell and increases in the more dilute half-cell until the two concentrations are equal; at that point $E_{\text{cell}} = 0$, and equilibrium has been reached. This equilibrium $[\text{Cu}^{2+}]$ is the same concentration that would have been formed if we had just mixed the two solutions directly to obtain a solution of intermediate concentration.

In any concentration cell, the spontaneous reaction is always in the direction that tends to equalize the concentrations.



21-21 The Relationship of E_{cell}^0 to ΔG^0 and K_{eq}

In Section 17-12 we studied the relationship between the standard Gibbs free energy change, ΔG^0 , and the thermodynamic equilibrium constant, K_{eq} .

$$\Delta G^0 = -RT \ln K_{\text{eq}}$$

There is also a simple relationship between ΔG^0 and the standard cell potential, E_{cell}^0 , for a redox reaction (reactants and products in standard states).

$$\Delta G^0 = -nFE_{\text{cell}}^0$$

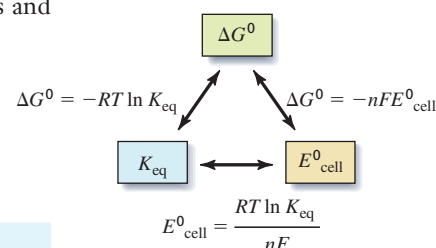
ΔG^0 can be thought of as the *negative of the maximum electrical work* that can be obtained from a redox reaction. In this equation, n is the number of moles of electrons transferred in the overall process (mol e^- /mol rxn), and F is the faraday, 96,485 J/V · mol e^- .

Combining these relationships for ΔG^0 gives the relationship between E_{cell}^0 values and equilibrium constants.

$$\underbrace{-nFE_{\text{cell}}^0}_{\Delta G^0} = \underbrace{-RT \ln K_{\text{eq}}}_{\Delta G^0}$$

After multiplying by -1 , we can rearrange.

$$nFE_{\text{cell}}^0 = RT \ln K_{\text{eq}} \quad \text{or} \quad E_{\text{cell}}^0 = \frac{RT \ln K_{\text{eq}}}{nF} \quad \text{or} \quad \ln K_{\text{eq}} = \frac{nFE_{\text{cell}}^0}{RT}$$

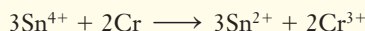


If any one of the three quantities ΔG^0 , K_{eq} , and E_{cell}^0 is known, the other two can be calculated using these equations. It is usually much easier to determine K_{eq} for a redox reaction from electrochemical measurements than by measuring equilibrium concentrations directly, as described in Chapter 17. Keep in mind the following for all redox reactions *at standard conditions*.

Forward Reaction	ΔG^0	K_{eq}	E_{cell}^0	
spontaneous (product-favored)	–	>1	+	} (all substances <i>at standard conditions</i>)
at equilibrium	0	1	0	
nonspontaneous (reactant-favored)	+	<1	–	

EXAMPLE 21-9 Calculation of ΔG^0 from Cell Potentials

Use tabulated standard electrode potentials to calculate the standard Gibbs free energy change, ΔG^0 , in J/mol at 25°C for the following reaction.

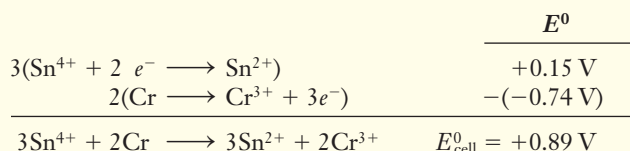


Plan

We evaluate the standard cell potential as we have done before. Then we apply the relationship $\Delta G^0 = -nFE_{\text{cell}}^0$.

Solution

The standard reduction potential for the $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple is +0.15 volt; that for the Cr^{3+}/Cr couple is –0.74 volt. The equation for the reaction shows Cr being oxidized to Cr^{3+} , so the sign of the E^0 value for the Cr^{3+}/Cr couple is reversed. The overall reaction, the sum of the two half-reactions, has a cell potential equal to the sum of the two half-reaction potentials.



► Recall from Chapter 15 that ΔG^0 can be expressed in joules per *mole of reaction*. Here we ask for the number of joules of free energy change that corresponds to the reaction of 2 moles of chromium with 3 moles of tin(IV) to give 3 moles of tin(III) ions and 2 moles of chromium(III) ions.

Unless otherwise noted, all content on this page is © Cengage Learning.

STOP & THINK

The negative value of ΔG^0 tells us that the standard reaction is spontaneous (product-favored), consistent with the positive value of E_{cell}^0 . This tells us nothing about the speed with which the reaction would occur.

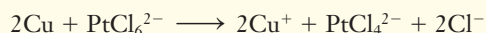
The positive value of E_{cell}^0 indicates that the forward reaction is spontaneous.

$$\begin{aligned}\Delta G^0 &= -nFE_{\text{cell}}^0 = -\left(\frac{6 \text{ mol } e^-}{\text{mol rxn}}\right)\left(\frac{9.65 \times 10^4 \text{ J}}{\text{V} \cdot \text{mol } e^-}\right)(+0.89 \text{ V}) \\ &= -5.2 \times 10^5 \text{ J/mol rxn} \quad \text{or} \quad -5.2 \times 10^2 \text{ kJ/mol rxn}\end{aligned}$$

You should now work Exercise 101.

EXAMPLE 21-10 Calculation of K_{eq} from Cell Potentials

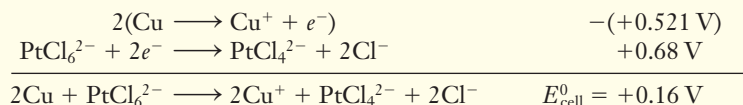
Use the standard cell potential to calculate the value of the equilibrium constant, K_{eq} , at 25°C for the following reaction.

**Plan**

We calculate E_{cell}^0 for the reaction as written. Then we use it to calculate K_{eq} .

Solution

First we find the appropriate half-reactions. As the equation is written, Cu is oxidized to Cu^+ , so we write the Cu^+/Cu couple as an oxidation and reverse the sign of its tabulated E^0 value. We balance the electron transfer and then add the half-reactions. The resulting E_{cell}^0 value can be used to calculate the equilibrium constant, K_{eq} , for the reaction *as written*.



Then we calculate K_{eq} .

$$\begin{aligned}\ln K_{\text{eq}} &= \frac{nFE_{\text{cell}}^0}{RT} = \frac{(2)(9.65 \times 10^4 \text{ J/V} \cdot \text{mol})(+0.16 \text{ V})}{(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = 12.5 \\ K_{\text{eq}} &= e^{12.5} = 2.7 \times 10^5\end{aligned}$$

$$\text{At equilibrium, } K_{\text{eq}} = \frac{[\text{Cu}^+]^2[\text{PtCl}_4^{2-}][\text{Cl}^-]^2}{[\text{PtCl}_6^{2-}]} = 2.7 \times 10^5.$$

The forward reaction is spontaneous, and the equilibrium lies far to the right.

You should now work Exercises 102 and 104.

STOP & THINK

As the problem is stated, we must keep the equation as written. We must therefore accept either a positive or a negative value of E_{cell}^0 . A negative value of E_{cell}^0 would lead to $K_{\text{eq}} < 1$.

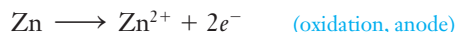
Primary Voltaic Cells

► We use batteries as portable sources of electrical energy in many ways—in flashlights, cell phones, notebook computers, calculators, automobiles, etc. A **battery** is a voltaic cell (or a set of voltaic cells coupled together) that has been designed for practical use.

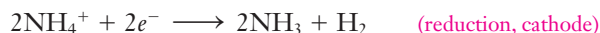
As any voltaic cell produces current (*discharges*), chemicals are consumed. **Primary voltaic cells** cannot be “recharged.” Once the chemicals have been consumed, further chemical action is not possible. The electrolytes or electrodes (or both) cannot be regenerated by reversing the current flow through the cell using an external direct current source. The most familiar examples of primary voltaic cells are the ordinary “dry” cells that are used as energy sources in flashlights and other small appliances.

21-22 Dry Cells

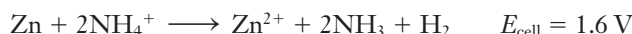
The first dry cell was patented by Georges Leclanché (1839–1882) in 1866, and such cells are still in common use. The container of the **Leclanché cell**, made of zinc, also serves as one of the electrodes (Figure 21-16). The other electrode is a carbon rod in the center of the cell. The zinc container is lined with porous paper to separate it from the other materials of the cell. The rest of the cell is filled with a moist mixture (the cell is not really dry) of ammonium chloride (NH_4Cl), manganese(IV) oxide (MnO_2), zinc chloride (ZnCl_2), and a porous, inert filler. Dry cells are sealed to keep the moisture from evaporating. As the cell operates (the electrodes must be connected externally), the metallic Zn is oxidized to Zn^{2+} , and the liberated electrons flow along the container to the external circuit. Thus, the zinc electrode is the anode (negative electrode).



The carbon rod is the cathode, at which ammonium ions are reduced.



Addition of the half-reactions gives the overall cell reaction



As H_2 is formed, it is oxidized by MnO_2 in the cell. This prevents collection of H_2 gas on the cathode, which would stop the reaction.

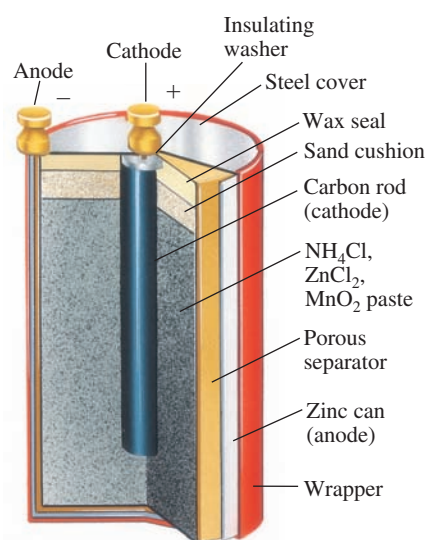


The ammonia produced at the cathode combines with zinc ions and forms a soluble compound containing the complex ions, $[\text{Zn}(\text{NH}_3)_4]^{2+}$.



This reaction reduces polarization due to the buildup of ammonia, and it keeps the concentration of Zn^{2+} from increasing substantially, which would decrease the cell potential by allowing it to diffuse away from the anode. Under heavy current conditions, NH_3 gas can build up in an ordinary dry cell slowing down the migration of the NH_4^+ ions to the cathode. This can cause a temporary reduction of the battery voltage and current, making

► The buildup of reaction products at an electrode is called **polarization** of the electrode.



A The Leclanché cell is a dry cell that generates a potential difference of about 1.6 volts.

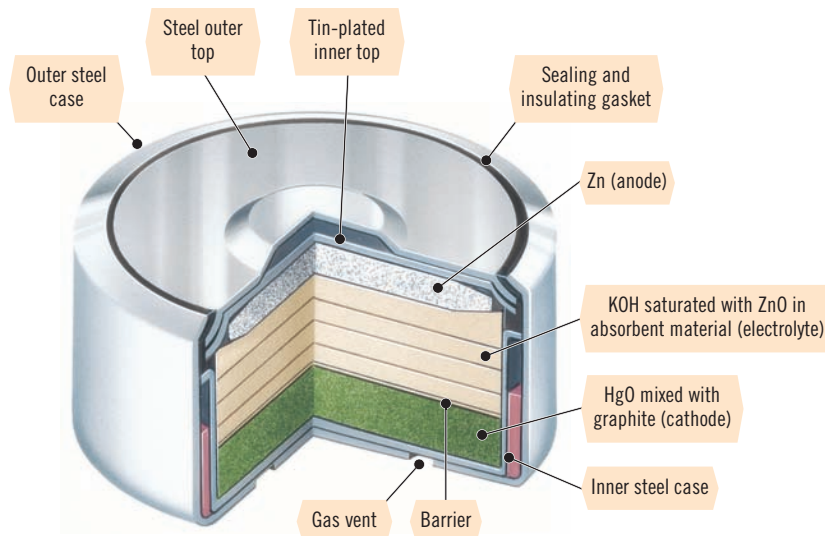
B Some commercial alkaline dry cells

Figure 21-16 Dry cells are actually moist on the inside with a paste of the oxidizing agent.

Unless otherwise noted, all content on this page is © Cengage Learning.



Charles D. Winters

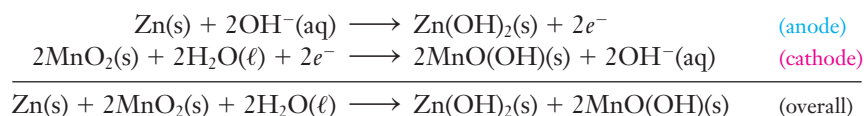


The mercury battery of the type frequently used in watches, calculators, and hearing aids is a primary cell. Although mercury in the water supply is known to cause health problems, no conclusive evidence has been found that the disposal of household batteries contributes to such problems. Nevertheless, manufacturers are working to decrease the amount of mercury in batteries. In recent years, the amount of mercury in alkaline batteries has decreased markedly; at the same time, the life of such batteries has increased dramatically.

it appear as if the battery is prematurely dying. On sitting, however, the NH_3 gas has time to react with the Zn^{2+} ions to form $[\text{Zn}(\text{NH}_3)_4]^{2+}$, which can diffuse away more readily from the cathode. Thus, a regular battery can often regain full power after sitting for a while after a period of heavy use. Once the reactant chemicals are sufficiently depleted, however, the battery is “dead.”

Alkaline dry cells are similar to Leclanché dry cells except that (1) the electrolyte is basic (alkaline) because it contains KOH, and (2) the interior surface of the Zn container is rough; this gives a larger surface area. Alkaline cells have a longer shelf life than ordinary dry cells, and they stand up better under heavy use. Alkaline batteries give considerably better performance because they do not involve the gas production (NH_3) that occurs in a regular NH_4Cl -based dry cell. The voltage of an alkaline cell is about 1.5 volts.

During discharge, the alkaline dry cell reactions are



Secondary Voltaic Cells

In **secondary voltaic cells**, or *reversible cells*, the original reactants can be regenerated. This is done by passing a direct current through the cell in the direction opposite of the discharge current flow. This process is referred to as *charging*, or recharging, a cell or battery. The most common example of a secondary voltaic cell is the lead storage battery used in most automobiles.

21-23 The Lead Storage Battery

The lead storage battery is depicted in Figure 21-17. One group of lead plates contains compressed spongy lead. These alternate with a group of lead plates composed of lead(IV) oxide, PbO_2 . The electrodes are immersed in a solution of about 40% sulfuric acid. When

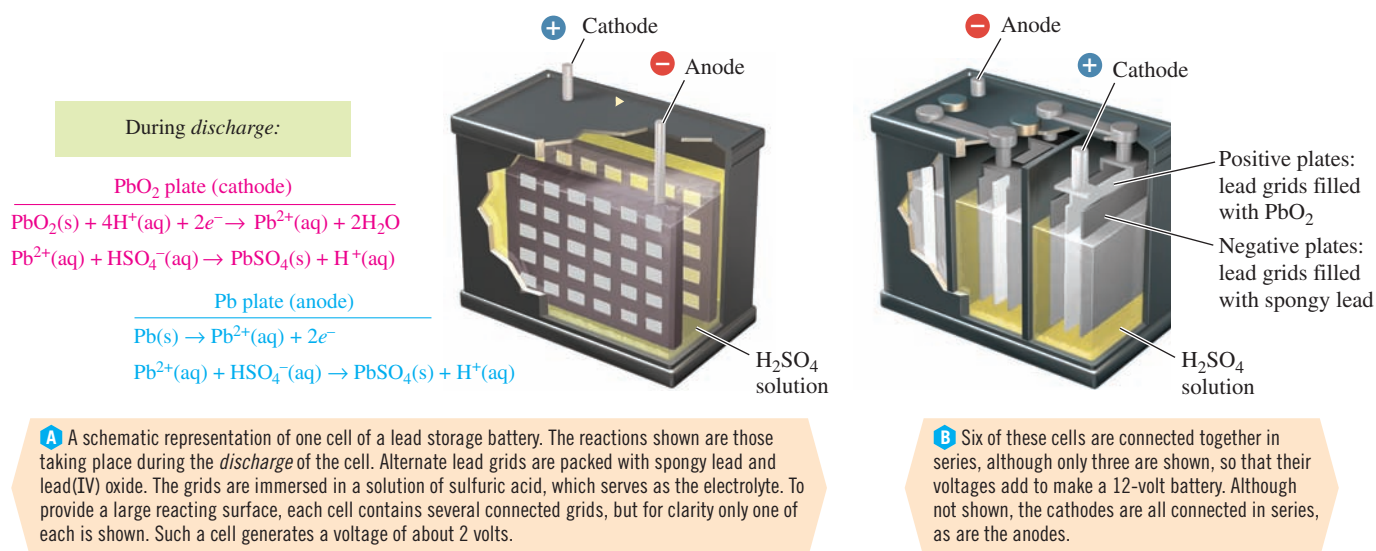
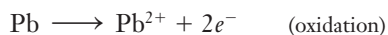


Figure 21-17 The lead storage battery, developed in 1859, is the oldest type of rechargeable battery. This is also called a lead-acid battery. Although not shown, the cathodes are all connected in series, as are the anodes.

the cell discharges, the spongy lead is oxidized to lead ions, and the lead plates accumulate a negative charge.



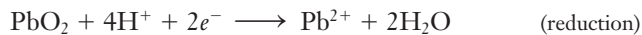
The lead ions then react with hydrogen sulfate ions from the sulfuric acid to form insoluble lead(II) sulfate. This coats the lead electrode.



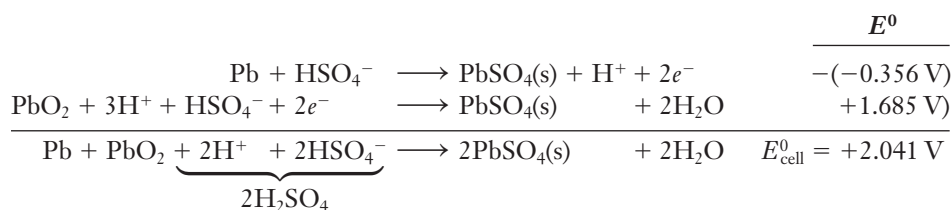
Thus, the net process at the anode *during discharge* is



The electrons travel through the external circuit and reenter the cell at the PbO_2 electrode, which is the cathode during discharge. Here, in the presence of hydrogen ions, the lead(IV) oxide is reduced to lead(II) ions, Pb^{2+} . These ions also react with HSO_4^- ions from the H_2SO_4 to form an insoluble PbSO_4 coating on the lead(IV) oxide electrode.



The net cell reaction for discharge and its standard potential are obtained by adding the net anode and cathode half-reactions and their tabulated potentials. The tabulated E^0 value for the anode half-reaction is reversed in sign because it occurs as oxidation during discharge.



► The decrease in the concentration of sulfuric acid provides an easy method for measuring the degree of discharge because the density of the solution decreases accordingly. We simply measure the density of the solution with a hydrometer.

One cell creates a potential of about 2 volts. Automobile 12-volt batteries have six cells connected in series. The potential declines only slightly during use, because solid reactants are being consumed. As the cell is used, some H_2SO_4 is consumed, lowering its concentration.

► A *generator* supplies direct current (dc). An *alternator* supplies alternating current (ac), so an electronic rectifier is used to convert this to direct current for the battery.



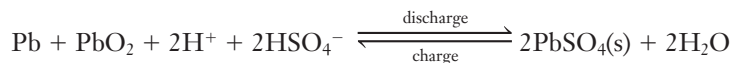
Charles D. Winters

Rechargeable nicad batteries are used to operate many electrical devices.

► To see why a nicad battery produces a constant voltage, write the Nernst equation for its reaction. Look at Q.

► The efficiency of energy conversion of the fuel cell operation is 60–70% of the theoretical maximum (based on ΔG). This represents about twice the efficiency that can be realized from burning hydrogen in a heat engine coupled to a generator.

When a potential slightly greater than the potential the battery can generate is imposed across the electrodes, the current flow can be reversed. The battery can then be recharged by reversing all the reactions. The alternator or generator applies this potential when the engine is in operation. The reactions that occur in a lead storage battery are summarized as follows.

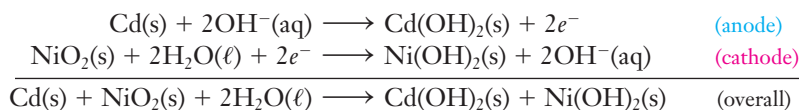


During many repeated charge–discharge cycles, some of the PbSO_4 falls to the bottom of the container and the H_2SO_4 concentration becomes correspondingly low. Eventually the battery cannot be recharged fully. It can be traded in for a new one, and the lead can be recovered and reused to make new batteries. This is one of the oldest and most successful examples of recycling.

21-24 The Nickel–Cadmium (Nicad) Cell

The nickel–cadmium (nicad) cell had widespread popularity from 1950 until recently because it can be recharged. It thus has a much longer useful life than ordinary (Leclanché) dry cells. Nicad batteries have been used in electronic toys, camcorders, and photographic equipment.

When the battery is delivering power the anode is cadmium, and the cathode is nickel(IV) oxide. The electrolytic solution is basic. The “discharge” reactions that occur in a nicad battery are

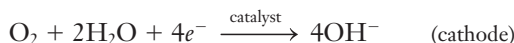


The solid reaction product at each electrode adheres to the electrode surface. Hence, a nicad battery can be recharged by an external source of electricity; that is, the electrode reactions can be reversed. Because no gases are produced by the reactions in a nicad battery, the unit can be sealed. The voltage of a nicad cell is about 1.4 volts, slightly less than that of a Leclanché cell. The toxicity of cadmium and the limited number of recharges that a nicad battery can handle before deactivating are problems that newer battery technologies have addressed. Nickel-metal-hydride (NiMH) and lithium-ion batteries are two newer generation cells that are environmentally friendlier, have longer lifetimes, and higher power-to-weight ratios. The European Union is phasing out the use of nicad batteries, which has increased the use and lowered the price of NiMH and Li-ion batteries worldwide.

21-25 The Hydrogen–Oxygen Fuel Cell

Fuel cells are voltaic cells in which the reactants are continuously supplied to the cell and the products are continuously removed. The hydrogen–oxygen fuel cell (Figure 21-18) already has many applications. It is used in spacecraft to supplement the energy obtained from solar cells. Liquid H_2 is carried on board as a propellant. The boiled-off H_2 vapor that ordinarily would be lost is used in a fuel cell to generate electrical power.

Hydrogen (the fuel) is supplied to the anode compartment. Oxygen is fed into the cathode compartment. The diffusion rates of the gases into the cell are carefully regulated for maximum efficiency. Oxygen is reduced at the cathode, which consists of porous carbon impregnated with a finely divided Pt or Pd catalyst.



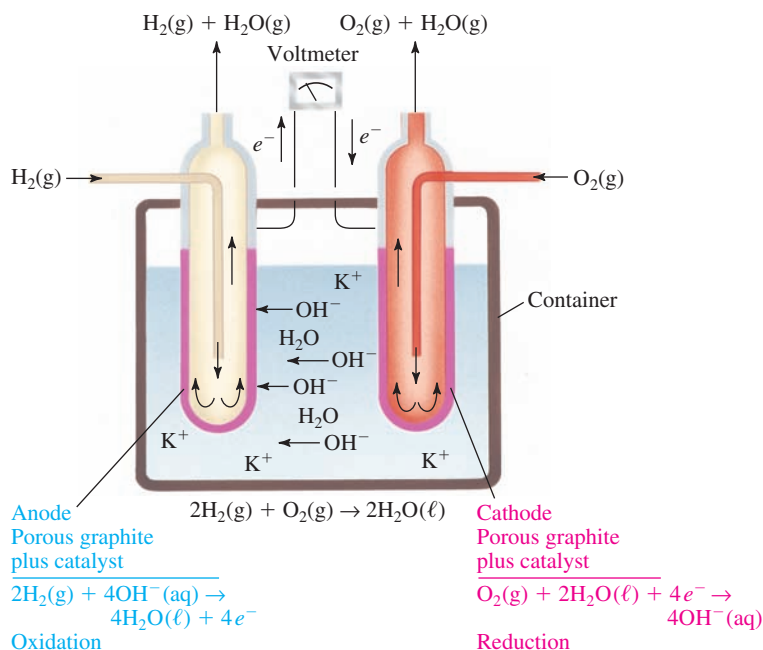
The OH^- ions migrate through the electrolyte to the anode, an aqueous solution of a base. The anode is also porous carbon containing a small amount of catalyst (Pt, Ag, or CoO). Here H_2 is oxidized to H_2O .



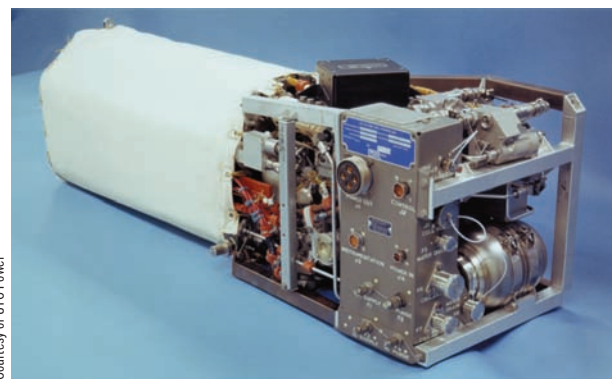
Courtesy of Ford Motor Company

Nickel-metal-hydride battery technology is used in hybrid gas–electric vehicles such as the Ford Escape Hybrid. The NiMH batteries (330-volt) are used to power the electric drive motor in the transmission. The batteries are recharged when brakes are applied via regenerative braking.

Unless otherwise noted, all content on this page is © Cengage Learning.



A The chemistry of a hydrogen-oxygen fuel cell

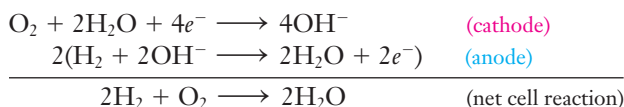


Courtesy of UTC Power

B Space shuttle fuel cells are self-contained units, each measuring $14 \times 15 \times 45$ in. and weighing 260 lb. Three of these are installed under the payload bay, just aft of the crew compartment, and are fueled by H_2 and O_2 from cryogenic tanks. Each fuel cell is capable of providing 12 kW continuously and up to 16 kW for short periods. A single unit can fully power the entire space shuttle in its day-to-day operation. The water produced is used for crew drinking and spacecraft cooling.

Figure 21-18 A hydrogen-oxygen fuel cell.

The net reaction is obtained from the two half-reactions.



The net reaction is the same as the burning of H_2 in O_2 to form H_2O , but combustion does not actually occur. Most of the chemical energy from the formation of $\text{H}-\text{O}$ bonds is converted directly into electrical energy, rather than into heat energy as in combustion.

When the H_2/O_2 fuel cell is used aboard spacecraft, it is operated at a high enough temperature that the water evaporates at the same rate as it is produced. The vapor is then condensed to pure water.

Current research is aimed at modifying the design of fuel cells to lower their cost. Better catalysts would speed the reactions to allow more rapid generation of electricity and produce more power per unit volume. The H_2/O_2 cell is nonpolluting; the only substance released is H_2O . Catalysts have been developed that allow sunlight to decompose water into hydrogen and oxygen, which might be used to operate fuel cells, permitting the utilization of solar energy.

Fuel cells have also been constructed using fuels other than hydrogen, such as methane or methanol. Biomedical researchers envision the possibility of using tiny fuel cells to operate pacemakers. The disadvantage of other power supplies for pacemakers, which are primary voltaic cells, is that their reactants are eventually consumed so that they require periodic surgical replacement. As long as the fuel and oxidizer are supplied, a fuel cell can—in theory, at least—operate forever. Eventually, tiny pacemaker fuel cells might be operated by the oxidation of blood sugar (the fuel) by the body's oxygen at a metal electrode implanted just below the skin.

Nathan S. Lewis/California Institute of Technology



Gaseous H_2 is produced from H_2O at an illuminated photoelectrode. Light from the sun may soon be used to produce hydrogen, the ultimate clean-burning fuel.

KEY TERMS

Alkaline cell A dry cell in which the electrolyte contains KOH.

Ampere Unit of electric current; 1 ampere equals 1 coulomb per second.

Anode The electrode at which oxidation occurs.

Battery A voltaic cell (or a set of voltaic cells coupled together) that has been designed for practical use.

Cathode The electrode at which reduction occurs.

Cathode protection Protection of a metal against corrosion by making it a cathode (attaching it to a sacrificial anode of a more easily oxidized metal).

Cell potential Potential difference, E_{cell} , between reduction and oxidation half-cells; may be at *nonstandard* conditions.

Concentration cell A voltaic cell in which the two half-cells are composed of the same species but contain different ion concentrations.

Corrosion Oxidation of metals in the presence of air and moisture.

Coulomb (C) Unit of electric charge; the amount of charge that passes a given point when 1 ampere of electric current flows for 1 second.

Coulometry The use of electrochemical cells to relate the amount of reactant or product to the amount of current passed through the cell.

Downs cell An electrolytic cell for the commercial electrolysis of molten sodium chloride.

Dry cells Ordinary batteries (voltaic cells) for flashlights, radios, and so on; many are Leclanché cells.

Electrochemistry The study of the chemical changes produced by electric current and the production of electricity by chemical reactions.

Electrode potentials Potentials, E , of half-reactions as reductions versus the standard hydrogen electrode.

Electrodes Surfaces on which oxidation and reduction half-reactions occur in electrochemical cells.

Electrolysis The process that occurs in electrolytic cells.

Electrolytic cell An electrochemical cell in which electrical energy causes a nonspontaneous (reactant-favored) redox reaction to occur.

Electrolytic conduction See *Ionic conduction*.

Electroplating Plating a metal onto a (cathodic) surface by electrolysis.

Faraday An amount of charge equal to 96,485 coulombs; corresponds to the charge associated with one mole of electrons, 6.022×10^{23} electrons.

Faraday's Law of Electrolysis The amount of substance that undergoes oxidation or reduction at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell.

Fuel cell A voltaic cell in which the reactants (usually gases) are supplied continuously and products are removed continuously.

Galvanic cell See *Voltaic cell*.

Glass electrode An electrode consisting of an AgCl-coated silver wire in contact with an HCl solution of known standard concentration (usually 1.00 M) in a thin-walled glass bulb; when immersed in a solution, this electrode develops a potential that is sensitive to the relative $[\text{H}^+]$ concentrations (and hence to pH differences) of the internal standard solution and the outside solution.

Half-cell The compartment in a voltaic cell in which the oxidation or reduction half-reaction occurs.

Hydrogen-oxygen fuel cell A fuel cell in which hydrogen is the fuel (reducing agent) and oxygen is the oxidizing agent.

Inert electrode An electrode that does not take part in the electrochemical reaction.

Ionic conduction Conduction of electric current by ions through a pure liquid or a solution; also known as *Electrolytic conduction*.

Lead storage battery A secondary voltaic cell that is used in most automobiles.

Leclanché cell A common type of dry cell (battery).

Metallic conduction Conduction of electric current through a metal or along a metallic surface.

Nernst equation An equation that corrects standard electrode potentials for nonstandard conditions.

Nickel-cadmium cell (nicad battery) A dry cell in which the anode is Cd, the cathode is NiO_2 , and the electrolyte is basic.

pH meter A device to measure the pH of a solution; typically consists of a pH-dependent glass electrode and a reference electrode (often a saturated calomel electrode).

Polarization of an electrode Buildup of a product of oxidation or reduction at an electrode, preventing further reaction.

Primary voltaic cell A voltaic cell that cannot be recharged; no further chemical reaction is possible once the reactants are consumed.

Sacrificial anode A more active metal that is attached to a less active metal to protect the less active metal cathode against corrosion.

Salt bridge A U-shaped tube containing an electrolyte that connects two half-cells of a voltaic cell.

Saturated calomel electrode An electrode that consists of a platinum wire in contact with a paste of liquid mercury and solid mercury(I) chloride, $\text{Hg}_2\text{Cl}_2(\text{s})$, all immersed in a saturated solution of potassium chloride, KCl; often used as the reference electrode in a pH meter.

Secondary voltaic cell A voltaic cell that can be recharged; the original reactants can be regenerated by reversing the direction of current flow.

Standard cell A cell in which all reactants and products are in their thermodynamic standard states (1 M for solution species and 1 atm partial pressure for gases).

Standard cell potential The potential difference, E_{cell}^0 , between standard reduction and oxidation half-cells.

Standard electrochemical conditions 1 M concentration for solution species, 1 atm partial pressure for gases, and pure solids and liquids.

Standard electrode A half-cell in which the oxidized and reduced forms of a species are present at unit activity: 1 M solutions of dissolved species, 1 atm partial pressure of gases, and pure solids and liquids.

Standard electrode potential By convention, the potential (E^0) of a half-reaction as a reduction relative to the standard hydrogen electrode, when all species are present at unit activity.

Standard hydrogen electrode (SHE) An electrode consisting of a platinum electrode that is immersed in a 1 M H^+ solution and that has H_2 gas bubbled over it at 1 atm pressure; defined

as the reference electrode, with a potential of *exactly* 0.0000 . . . volts.

Voltage Potential difference between two electrodes; a measure of the chemical potential for a redox reaction to occur.

Voltaic cell An electrochemical cell in which a spontaneous (product-favored) chemical reaction produces electricity; also known as a *galvanic cell*.

EXERCISES

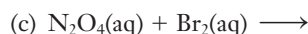
● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Redox Review and General Concepts

- (a) Define oxidation and reduction in terms of electron gain or loss. (b) What is the relationship between the numbers of electrons gained and lost in a redox reaction? (c) Do all electrochemical cells involve redox reactions?
- Define and illustrate (a) oxidizing agent, and (b) reducing agent.
- For each of the following unbalanced equations, (i) write the half-reactions for oxidation and for reduction, and (ii) balance the overall equation in acidic solution using the half-reaction method. (See Sections 11-4 and 11-5.)
 - $\text{Hg}^{2+} + \text{Sn} \longrightarrow \text{Hg} + \text{Sn}^{2+}$ (acidic solution)
 - $\text{MnO}_2 + \text{Cl}^- \longrightarrow \text{Mn}^{2+} + \text{Cl}_2$ (acidic solution)
 - $\text{Sn}^{2+} + \text{O}_2 \longrightarrow \text{Sn}^{4+} + \text{H}_2\text{O}$ (acidic solution)
- For each of the following unbalanced equations, (i) write the half-reactions for oxidation and reduction, and (ii) balance the overall equation using the half-reaction method. (See Sections 11-4 and 11-5.)
 - $\text{FeS} + \text{NO}_3^- \longrightarrow \text{NO} + \text{SO}_4^{2-} + \text{Fe}^{2+}$ (acidic solution)
 - $\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} \longrightarrow \text{Cr}^{3+} + \text{Fe}^{3+}$ (acidic solution)
 - $\text{S}^{2-} + \text{Cl}_2 + \text{OH}^- \longrightarrow \text{SO}_4^{2-} + \text{Cl}^- + \text{H}_2\text{O}$ (basic solution)
- (a) Compare and contrast ionic conduction and metallic conduction. (b) What is an electrode? (c) What is an inert electrode?
- Support or refute each of the following statements:
 - In any electrochemical cell, the positive electrode is the one toward which the electrons flow through the wire.
 - The cathode is the negative electrode in any electrochemical cell.
- For each of the following unbalanced equations, (i) write the half-reactions for oxidation and reduction, (ii) identify the species that lose and the species that gain electrons, and (iii) write the balanced net ionic equation for the overall reaction. (See Sections 11-4 and 11-5.)
 - $\text{Cr(s)} + \text{Au}^{3+}(\text{aq}) \longrightarrow \text{Cr}^{2+}(\text{aq}) + \text{Au(s)}$
 - $\text{NO}_2^-(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) \longrightarrow \text{NO}_3^-(\text{aq}) + \text{Cr}^{3+}(\text{aq})$ (acidic solution)



$\text{NO}_2^-(\text{aq}) + \text{Br}^-(\text{aq})$ (basic solution)

- Balance the following redox equations. All occur in basic solution. (See Sections 11-4 and 11-5.)
 - $\text{Al(s)} + \text{OH}^-(\text{aq}) \longrightarrow \text{Al(OH)}_4^-(\text{aq}) + \text{H}_2(\text{g})$
 - $\text{CrO}_4^{2-}(\text{aq}) + \text{SO}_3^{2-}(\text{aq}) \longrightarrow \text{Cr(OH)}_3(\text{s}) + \text{SO}_4^{2-}(\text{aq})$
 - $\text{Zn(s)} + \text{Cu(OH)}_2(\text{s}) \longrightarrow [\text{Zn(OH)}_4]^{2-}(\text{aq}) + \text{Cu(s)}$
 - $\text{HS}^-(\text{aq}) + \text{ClO}_3^-(\text{aq}) \longrightarrow \text{S(s)} + \text{Cl}^-(\text{aq})$

Electrolytic Cells: General Concepts

- (a) Solids such as potassium bromide, KBr, and sodium nitrate, NaNO₃, do not conduct electric current even though they are ionic. Why? Can these substances be electrolyzed as solids? (b) Support or refute the statement that the Gibbs free energy change, ΔG , is positive for any electrolysis reaction.
- (a) Metallic magnesium cannot be obtained by electrolysis of aqueous magnesium chloride, MgCl₂. Why? (b) There are no sodium ions in the overall cell reaction for the electrolysis of aqueous sodium chloride. Why?
- Consider the electrolysis of molten aluminum oxide, Al₂O₃, dissolved in cryolite, Na₃AlF₆, with inert electrodes. This is the Hall-Héroult process for commercial production of aluminum (Section 26-6). The following experimental observations can be made when current is supplied: (i) Silvery metallic aluminum is produced at one electrode. (ii) Oxygen, O₂, bubbles off at the other electrode. Diagram the cell, indicating the anode, the cathode, the positive and negative electrodes, the half-reaction occurring at each electrode, the overall cell reaction, and the direction of electron flow through the wire.
- Do the same as in Exercise 11 for the electrolysis of molten calcium chloride with inert electrodes. The following observations are made when current is supplied:
 - Bubbles of pale green chlorine gas, Cl₂, are produced at one electrode.
 - Silvery-white molten metallic calcium is produced at the other electrode.
- Do the same as in Exercise 11 for the electrolysis of aqueous potassium sulfate, K₂SO₄. The following observations are made when current is supplied: (i) Bubbles of gaseous hydrogen are produced at one electrode, and the solution becomes more basic around that electrode. (ii) Bubbles of

● **Molecular Reasoning** exercises

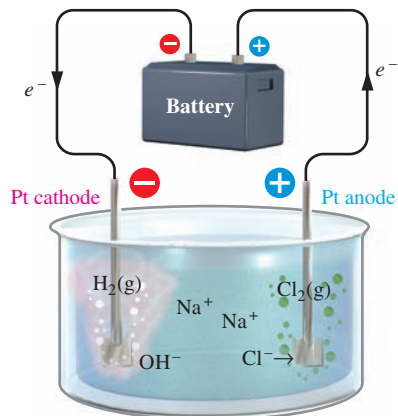
▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

gaseous oxygen are produced at the other electrode, and the solution becomes more acidic around that electrode.

14. In the electrolysis of aqueous sodium chloride, NaCl, shown below, what are the half-reactions that occur at each electrode?



15. (a) Write the equation for the half-reaction when H_2O is reduced in an electrochemical cell. (b) Write the equation for the half-reaction when H_2O is oxidized in an electrochemical cell. (c) Write the equation for the electrolysis of water.

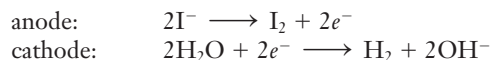


Charles D. Winters

Electrolysis of water

16. Define (a) a coulomb, (b) an electric current, (c) an ampere, and (d) a faraday.
17. Calculate the number of electrons that have a total charge of 1 coulomb.
18. For each of the following cations, calculate (i) the number of faradays required to produce 1.00 mol of free metal and (ii) the number of coulombs required to produce 1.00 g of free metal. (a) Fe^{3+} ; (b) Sn^{2+} ; (c) Hg_2^{2+}
19. For each of the following cations, calculate (i) the number of faradays required to produce 1.00 mol of free metal, and (ii) the number of coulombs required to produce 1.00 g of free metal. (a) Fe^{2+} ; (b) Au^{3+} ; (c) K^+
20. In 400. min, 2.25 g of copper is obtained by electrolysis of a copper(I) acetate solution. (a) How many amperes is required for this experiment? (b) Using the same current and time, what mass of copper would be obtained from a copper(II) nitrate solution?

21. A mass of 1.20 g of silver is plated from a silver nitrate solution in 1.25 h. Calculate the (a) coulombs, (b) faradays, and (c) amperes necessary for this process.
22. Rhodium is an element that has the appearance of silver, but it does not tarnish like silver and, because it is very hard, does not become worn or scratched like silver. What mass of rhodium could be plated by electrolysis of a $\text{Rh}(\text{NO}_3)_3$ solution with a 0.755-A current for 15.0 min?
23. Hydrogen may be the fuel of the future for automobiles, according to some experts. Hydrogen can be isolated from water by electrolysis. Calculate the mass of hydrogen that is released when a 1.50-A current is passed through salt water for 12.75 h.
24. The mass of silver deposited on a spoon during electroplating was 0.976 mg. How much electric charge passed through the cell?
25. What mass of platinum could be plated onto a ring from the electrolysis of a platinum(II) salt with a 0.415-A current for 195 s?
26. What mass of silver could be plated onto a spoon from electrolysis of silver nitrate with a 2.78-A current for 45.0 min?
27. ● ▲ We pass enough current through a solution to plate out *one* mole of nickel metal from a solution of NiSO_4 . In other electrolysis cells, this same current plates out *two* moles of silver from AgNO_3 solution but liberates only *one-half* mole of O_2 gas. Explain these observations.
28. ▲ A current is passed through 500. mL of a solution of CaI_2 . The following electrode reactions occur:



After some time, analysis of the solution shows that 41.5 mmol of I_2 has been formed. (a) How many faradays of charge have passed through the solution? (b) How many coulombs? (c) What volume of dry H_2 at STP has been formed? (d) What is the pH of the solution?

29. The cells in an automobile battery were charged at a steady current of 5.0 A for exactly 1.75 h. What masses of Pb and PbO_2 were formed in each cell? The overall reaction is
- $$2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\ell) \longrightarrow \text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq})$$



Charles D. Winters

30. ▲ The chemical equation for the electrolysis of a fairly concentrated brine solution is
- $$2\text{NaCl}(\text{aq}) + 2\text{H}_2\text{O}(\ell) \longrightarrow \text{Cl}_2(\text{g}) + \text{H}_2(\text{g}) + 2\text{NaOH}(\text{aq})$$

What volume of gaseous chlorine would be generated at 752 torr and 15°C if the process were 85% efficient and if a current of 1.70 A flowed for 5.00 h?

31. An electrolytic cell contains 50.0 mL of a 0.165 *M* solution of FeCl₃. A current of 0.665 A is passed through the cell, causing deposition of Fe(s) at the cathode. What is the concentration of Fe³⁺(aq) in the cell after this current has run for 20.0 min?
32. Suppose 250. mL of a 0.455 *M* solution of CuCl₂ is electrolyzed. How long will a current of 0.750 A have to run in order to reduce the concentration of Cu²⁺ to 0.167 *M*? What mass of Cu(s) will be deposited on the cathode during this time?
33. One method for recovering metals from their ores is by electrodeposition. For example, after passing a current of 18.0 amps through a molten tantalum salt for 38.0 min, workers at a metals processing plant isolated 15.4 g of pure tantalum. What was the oxidation state of tantalum in the molten material from which the metal was isolated?
34. ▲ Three electrolytic cells are connected in series; that is, the same current passes through all three, one after another. In the first cell, 1.20 g of Cd is oxidized to Cd²⁺; in the second, Ag⁺ is reduced to Ag; in the third, Fe²⁺ is oxidized to Fe³⁺. (a) Find the number of faradays passed through the circuit. (b) What mass of Ag is deposited at the cathode in the second cell? (c) What mass of Fe(NO₃)₃ could be recovered from the solution in the third cell?

Voltaic Cells: General Concepts

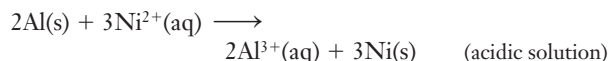
35. What does voltage measure? How does it vary with time in a primary voltaic cell? Why?
36. ● (a) Why must the solutions in a voltaic cell be kept separate and not allowed to mix? (b) What are the functions of a salt bridge?
37. A voltaic cell containing a standard Fe³⁺/Fe²⁺ electrode and a standard Ga³⁺/Ga electrode is constructed, and the circuit is closed. Without consulting the table of standard reduction potentials, diagram and completely describe the cell from the following experimental observations. (i) The mass of the gallium electrode decreases, and the gallium ion concentration increases around that electrode. (ii) The ferrous ion, Fe²⁺, concentration increases in the other electrode solution.
38. Repeat Exercise 37 for a voltaic cell that contains standard Co²⁺/Co and Au³⁺/Au electrodes. The observations are: (i) Metallic gold plates out on one electrode, and the gold ion concentration decreases around that electrode. (ii) The mass of the cobalt electrode decreases, and the cobalt(II) ion concentration increases around that electrode.
39. Write the shorthand notation for the cell described in Exercise 37.
40. Write the shorthand notation for the cell described in Exercise 38.
41. ● Appendix J lists selected reduction potentials in volts at 25°C. Why is it not necessary to list a mixture of reduction and oxidation potentials?
42. ▲ In Section 6-8 we learned how to predict from the activity series (Table 6-10) which metals replace which

others from aqueous solutions. From that table, we predict that nickel will displace silver. The equation for this process is



Suppose we set up a voltaic cell based on this reaction.

- (a) What half-reaction would represent the reduction in this cell? (b) What half-reaction would represent the oxidation? (c) Which metal would be the anode? (d) Which metal would be the cathode? (e) Diagram this cell.
43. A cell is constructed by immersing a strip of iron in a 1.0 *M* Fe(NO₃)₂ solution and a strip of gold in a 1.0 *M* AuNO₃ solution. The circuit is completed by a wire and a salt bridge. As the cell operates, the strip of gold gains mass (only gold), and the concentration of gold ions in the solution around the gold strip decreases, while the strip of iron loses mass, and the concentration of iron ions increases in the solution around the iron strip. Write the equations for the half-reactions that occur at the cathode and at the anode.
44. ● When metallic copper is placed into aqueous silver nitrate, a spontaneous redox reaction occurs. No electricity is produced. Why?
45. Assume that a voltaic cell utilizes the redox reaction



Potassium and nitrate ions may also be present. Draw this voltaic cell, and label the anode, cathode, electron flow, and ion flow.

46. Assume that a voltaic cell, proposed as a method for the purification of uranium, utilizes the redox reaction
- $$3\text{Mg(s)} + 2\text{U}^{3+}(\text{aq}) \longrightarrow 3\text{Mg}^{2+}(\text{aq}) + 2\text{U(s)} \quad (\text{acidic solution})$$

Potassium and nitrate ions may also be present. Draw this voltaic cell, and label the anode, cathode, electron flow, and ion flow.

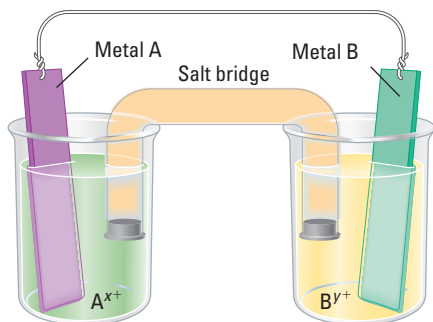
Standard Cell Potentials

47. (a) What are standard electrochemical conditions? (b) Why are we permitted to assign arbitrarily an electrode potential of exactly 0 V to the standard hydrogen electrode?
48. What does the sign of the standard reduction potential of a half-reaction indicate? What does the magnitude indicate?
49. (a) What are standard reduction potentials? (b) What information is contained in tables of standard reduction potentials (Tables 21-2 and 21-3, Appendix J)? How is the information in such tables arranged?
50. Standard reduction potentials are 1.36 V for Cl₂(g)/Cl⁻, 0.799 V for Ag⁺/Ag(s), 0.521 V for Cu⁺/Cu(s), 0.337 V for Cu²⁺/Cu(s), -0.44 V for Fe²⁺/Fe(s), -2.71 V for Na⁺/Na(s), and -2.925 V for K⁺/K(s). (a) Arrange the oxidizing agents in order of increasing strength. (b) Which of these oxidizing agents will oxidize Cu under standard-state conditions?



51. Standard reduction potentials are 1.455 V for the $\text{PbO}_2(\text{s})/\text{Pb}(\text{s})$ couple, 2.87 V for $\text{F}_2(\text{g})/\text{F}^-$, 3.06 V for $\text{F}_2(\text{g})/\text{HF}(\text{aq})$, and 1.77 V for $\text{H}_2\text{O}_2(\text{aq})/\text{H}_2\text{O}(\ell)$. Under standard-state conditions, (a) which is the strongest oxidizing agent, (b) which oxidizing agent(s) could oxidize lead to lead(IV) oxide, and (c) which oxidizing agent(s) could oxidize fluoride ion in an acidic solution?
52. Arrange the following less commonly encountered metals in an activity series from the most active to the least active: radium $[\text{Ra}^{2+}/\text{Ra}(\text{s}), E^0 = -2.9 \text{ V}]$, rhodium $[\text{Rh}^{3+}/\text{Rh}(\text{s}), E^0 = 0.80 \text{ V}]$, europium $[\text{Eu}^{2+}/\text{Eu}(\text{s}), E^0 = -3.4 \text{ V}]$. How do these metals compare in reducing ability with the active metal lithium $[\text{Li}^+/\text{Li}(\text{s}), E^0 = -3.0 \text{ V}]$, with hydrogen, and with platinum $[\text{Pt}^{2+}/\text{Pt}(\text{s}), E^0 = 1.2 \text{ V}]$, which is a noble metal and one of the least active of the metals?
53. Using the list of standard electrode potentials, order the following by decreasing strength as an oxidizing agent (strongest first, weakest last): dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$), hydrogen peroxide (H_2O_2), lead(IV) oxide (PbO_2), nitrate ion (NO_3^-), and permanganate ion (MnO_4^-).
54. Diagram the following cells. For each cell, write the balanced equation for the reaction that occurs spontaneously, and calculate the cell potential. Indicate the direction of electron flow, the anode, the cathode, and the polarity (+ or -) of each electrode. In each case, assume that the circuit is completed by a wire and a salt bridge.
- (a) A strip of magnesium is immersed in a solution that is 1.0 M in Mg^{2+} , and a strip of silver is immersed in a solution that is 1.0 M in Ag^+ . (b) A strip of zinc is immersed in a solution that is 1.0 M in Zn^{2+} , and a strip of tin is immersed in a solution that is 1.0 M in Sn^{2+} .
55. Repeat Exercise 54 for the following cells. (a) A strip of chromium is immersed in a solution that is 1.0 M in Cr^{3+} , and a strip of gold is immersed in a solution that is 1.0 M in Au^{3+} . (b) A strip of aluminum is immersed in a solution that is 1.0 M in Al^{3+} , and a strip of lead is immersed in a solution that is 1.0 M in Pb^{2+} .

For Exercises 56, 57, 88, and 89, draw a cell similar to the one shown here with the anode on the left and the cathode on the right. Identify metal A, metal B, solution A, and solution B. Write the balanced equation for the reaction that occurs spontaneously. Calculate the cell potential and write the shorthand notation for the cell. Indicate the direction of electron flow, the anode, the cathode, and the polarity (+ or -) of each electrode.



56. (See the directions above.) A standard magnesium and aluminum cell.
57. (See directions preceding Exercise 56.) A standard cadmium and zinc cell.

In answering Exercises 58–77, justify each answer by appropriate calculations. Assume that each reaction occurs at standard electrochemical conditions.

58. (a) Will Fe^{3+} oxidize Sn^{2+} to Sn^{4+} in acidic solution? (b) Will dichromate ions oxidize fluoride ions to free fluorine in acidic solution?
59. (See directions preceding Exercise 58.) (a) Will dichromate ions oxidize arsenous acid, H_3AsO_3 , to arsenic acid, H_3AsO_4 , in acid solution? (b) Will dichromate ions oxidize hydrogen peroxide, H_2O_2 , to free oxygen, O_2 , in acidic solution?
60. (See directions preceding Exercise 58.) (a) Will permanganate ions oxidize Cr^{3+} to $\text{Cr}_2\text{O}_7^{2-}$ in acidic solution? (b) Will sulfate ions oxidize arsenous acid, H_3AsO_3 , to arsenic acid, H_3AsO_4 , in acid solution?
61. (See directions preceding Exercise 58.) Calculate the standard cell potential, E_{cell}^0 , for the cell described in Exercise 37.
62. (See directions preceding Exercise 58.) Calculate the standard cell potential, E_{cell}^0 , for the cell described in Exercise 38.
63. (See directions preceding Exercise 58.) (a) Write the equation for the oxidation of $\text{Zn}(\text{s})$ by $\text{Br}_2(\ell)$. (b) Calculate the potential of this reaction under standard-state conditions. (c) Is this a spontaneous reaction?
64. (See directions preceding Exercise 58.) For each of the following cells, (i) write the net reaction in the direction consistent with the way the cell is written, (ii) write the half-reactions for the anode and cathode processes, (iii) find the standard cell potential, E_{cell}^0 , at 25°C, and (iv) state whether the standard cell reaction actually occurs as given or in the reverse direction.
- (a) $\text{Cr} | \text{Cr}^{3+} || \text{Cu}^{2+} | \text{Cu}$
 (b) $\text{Ag} | \text{Ag}^+ || \text{Cd}^{2+} | \text{Cd}$
65. (See directions preceding Exercise 58.) Repeat Exercise 64 for the following cells:
- (a) $\text{Al} | \text{Al}^{3+} || \text{Ce}^{4+}, \text{Ce}^{3+} | \text{Pt}$
 (b) $\text{Zn} | \text{Zn}^{2+} || \text{Tl}^+ | \text{Tl}$
66. (See directions preceding Exercise 58.) Which of the following reactions are spontaneous in voltaic cells under standard conditions?
- (a) $\text{H}_2(\text{g}) \longrightarrow \text{H}^+(\text{aq}) + \text{H}^-(\text{aq})$
 (b) $\text{Zn}(\text{s}) + 4\text{CN}^-(\text{aq}) + \text{Ag}_2\text{CrO}_4(\text{s}) \longrightarrow \text{Zn}(\text{CN})_4^{2-}(\text{aq}) + 2\text{Ag}(\text{s}) + \text{CrO}_4^{2-}(\text{aq})$
 (c) $\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{Sr}(\text{s}) \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\ell) + \text{Sr}^{2+}(\text{aq})$
 (d) $\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\ell) + \text{ZnS}(\text{s}) \longrightarrow 2\text{HOCl}(\text{aq}) + \text{H}_2\text{S}(\text{aq}) + \text{Zn}(\text{s})$
67. (See directions preceding Exercise 58.) Consult a table of standard reduction potentials, and determine which of the following reactions are spontaneous under standard electrochemical conditions.
- (a) $\text{Mn}(\text{s}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{H}_2(\text{g}) + \text{Mn}^{2+}(\text{aq})$
 (b) $2\text{Al}^{3+}(\text{aq}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{Al}(\text{s}) + 6\text{H}^+(\text{aq})$

- (c) $2\text{Cr}(\text{OH})_3(\text{s}) + 6\text{F}^-(\text{aq}) \longrightarrow 2\text{Cr}(\text{s}) + 6\text{OH}^-(\text{aq}) + 3\text{F}_2(\text{g})$
- (d) $\text{Cl}_2(\text{g}) + 2\text{Br}^-(\text{aq}) \longrightarrow \text{Br}_2(\ell) + 2\text{Cl}^-(\text{aq})$
68. (See directions preceding Exercise 58.) Which of each pair is the stronger reducing agent? (a) Ag or H_2 ; (b) Sn or Pb; (c) Hg or Au; (d) Cl^- in acidic solution or Cl^- in basic solution; (e) HCl or H_2S ; (f) Ag or Au
69. (See directions preceding Exercise 58.) Which of each pair is the stronger oxidizing agent? (a) Cu^+ or Ag^+ ; (b) Sn^{2+} or Sn^{4+} ; (c) Fe^{2+} or Fe^{3+} ; (d) I_2 or Br_2 ; (e) MnO_4^- in acidic solution or MnO_4^- in basic solution; (f) H^+ or Co^{2+}
70. ▲ (See directions preceding Exercise 58.) The element ytterbium forms both 2+ and 3+ cations in aqueous solution. $E^\circ = -2.797 \text{ V}$ for $\text{Yb}^{2+}/\text{Yb}(\text{s})$, and -2.267 V for $\text{Yb}^{3+}/\text{Yb}(\text{s})$. What is the standard-state reduction potential for the $\text{Yb}^{3+}/\text{Yb}^{2+}$ couple?
71. ▲ (See directions preceding Exercise 58.) The standard reduction potential for Cu^+ to $\text{Cu}(\text{s})$ is 0.521 V , and for Cu^{2+} to $\text{Cu}(\text{s})$ it is 0.337 V . Calculate the E° value for the $\text{Cu}^{2+}/\text{Cu}^+$ couple.
72. (See directions preceding Exercise 58.) Consider the suggestion for purifying uranium without an external energy source by setting up a voltaic cell with the reaction
- $$3\text{Mg}(\text{s}) + 2\text{U}^{3+}(\text{aq}) \longrightarrow 3\text{Mg}^{2+}(\text{aq}) + 2\text{U}(\text{s}) \quad (\text{acidic solution})$$

The standard reduction potentials are -1.798 for the uranium half-reaction and -2.37 for the magnesium half-reaction. (a) Will this setup work spontaneously? (b) Calculate the voltage produced by this cell as written.

73. (See directions preceding Exercise 58.) A reaction is proposed for a nickel–cadmium battery as $\text{Ni}(\text{s}) + \text{Cd}^{2+}(\text{aq}) \longrightarrow \text{Ni}^{2+}(\text{aq}) + \text{Cd}(\text{s})$. (a) Is the reaction spontaneous as written? (b) Calculate the voltage produced by this voltaic cell as written.
74. (See directions preceding Exercise 58.) Selecting from half-reactions involving the following species, write the spontaneous reaction that will produce the voltaic cell with the highest voltage in an acidic solution: K^+ , Ca^{2+} , Ni^{2+} , H_2O_2 , and F_2 .
75. (See directions preceding Exercise 58.) Propose the spontaneous reaction that will produce the voltaic cell with the highest voltage output by choosing from only reduction and oxidation potentials involving: Au^{3+} and Au^+ , HgO and Hg , Ag_2O and Ag , S and S^{2-} , and SO_4^{2-} and SO_3^{2-} .
76. ● (See directions preceding Exercise 58.) Tarnished silver is coated with a layer of $\text{Ag}_2\text{S}(\text{s})$. The coating can be removed by boiling the silverware in an aluminum pan, with some baking soda or salt added to make the solution conductive. Explain this from the point of view of electrochemistry.
77. ● ▲ (See directions preceding Exercise 58.) Describe the process of corrosion. How can corrosion of an easily oxidizable metal be prevented if the metal must be exposed to the weather?

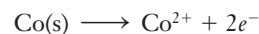
Concentration Effects; Nernst Equation

For cell voltage calculations, assume that the temperature is 25°C unless stated otherwise.

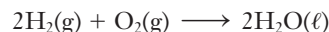
78. ▲ Describe how the Nernst equation is important in electrochemistry. How would the Nernst equation be modified if we wished to use natural logarithms, $\ln$? What is the value of the constant in the following equation at 25°C ?

$$E = E^\circ - \frac{\text{constant}}{n} \ln Q$$

79. Identify all of the terms in the Nernst equation. What part of the Nernst equation represents the correction factor for nonstandard electrochemical conditions?
80. By putting the appropriate values into the Nernst equation, show that it predicts that the voltage of a standard half-cell is equal to E° . Use the Zn^{2+}/Zn reduction half-cell as an illustration.
81. Calculate the potential associated with the following half-reaction when the concentration of the cobalt(II) ion is $1.0 \times 10^{-3} \text{ M}$.

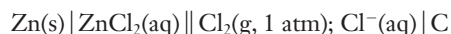


82. Consider the voltaic cell
- $$2\text{Ag}^+(\text{aq}) + \text{Cd}(\text{s}) \longrightarrow 2\text{Ag}(\text{s}) + \text{Cd}^{2+}(\text{aq})$$
- operating at 298 K .
- (a) What is the E° for this cell?
- (b) If $[\text{Cd}^{2+}] = 2.0 \text{ M}$ and $[\text{Ag}^+] = 0.25 \text{ M}$, what is E_{cell} ?
- (c) If $E_{\text{cell}} = 1.25 \text{ V}$ and $[\text{Cd}^{2+}] = 0.100 \text{ M}$, what is $[\text{Ag}^+]$?
83. The standard reduction potentials for the $\text{H}^+/\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$, $\text{H}^+/\text{H}_2\text{O}(\ell)$ couples are 0.0000 V and 1.229 V , respectively. (a) Write the half-reactions and the overall reaction, and calculate E° for the reaction



- (b) Calculate E for the cell when the pressure of H_2 is 2.85 atm and that of O_2 is 1.20 atm .

84. Consider the cell represented by the notation



Calculate (a) E° , and (b) E for the cell when the concentration of the ZnCl_2 is 0.35 mol/L and the Cl_2/Cl^- half-cell is at standard conditions.

85. What is the concentration of Ag^+ in a half-cell if the reduction potential of the Ag^+/Ag couple is observed to be 0.40 V ?
86. What must be the pressure of fluorine gas in order to produce a half-cell reduction potential of the F_2/F^- couple of 2.70 V in a solution that contains 0.34 M F^- ?
87. Calculate the cell potential of each of the following electrochemical cells at 25°C .
- (a) $\text{Sn}(\text{s}) | \text{Sn}^{2+}(7.0 \times 10^{-3} \text{ M}) || \text{Ag}^+(0.110 \text{ M}) | \text{Ag}(\text{s})$
- (b) $\text{Zn}(\text{s}) | \text{Zn}^{2+}(0.500 \text{ M}) || \text{Fe}^{3+}(7.2 \times 10^{-6} \text{ M}), \text{Fe}^{2+}(0.20 \text{ M}) | \text{Pt}$
- (c) $\text{Pt} | \text{H}_2(1 \text{ atm}) | \text{HCl}(0.00880 \text{ M}) | \text{Cl}_2(1 \text{ atm}) | \text{Pt}$



88. (See the directions preceding Exercise 56.) Draw the cell represented by Exercise 87(a) and label its components.
89. (See the directions preceding Exercise 56.) Draw the cell represented by Exercise 87(c) and label its components.
90. Calculate the cell potential of each of the following electrochemical cells at 25°C.
- (a) $\text{Pt} | \text{H}_2(8.00 \text{ atm}), \text{H}^+(1.00 \times 10^{-3} \text{ M}) || \text{Ag}^+(0.00549 \text{ M}) | \text{Ag(s)}$
- (b) $\text{Pt} | \text{H}_2(1.00 \text{ atm}), \text{H}^+(\text{pH} = 5.97) || \text{H}^+(\text{pH} = 3.47), \text{H}_2(1.00 \text{ atm}) | \text{Pt}$
- (c) $\text{Pt} | \text{H}_2(0.0361 \text{ atm}), \text{H}^+(0.0175 \text{ M}) || \text{H}^+(0.0175 \text{ M}), \text{H}_2(5.98 \times 10^{-4} \text{ atm}) | \text{Pt}$
91. ▲ Find the potential of the cell in which identical iron electrodes are placed into solutions of FeSO_4 of concentration 1.5 mol/L and 0.15 mol/L.
92. What is the cell potential of a concentration cell that contains two hydrogen electrodes if the cathode contacts a solution with $\text{pH} = 7.8$ and the anode contacts a solution with $[\text{H}^+] = 0.05 \text{ M}$?
93. ▲ We construct a standard copper–cadmium cell, close the circuit, and allow the cell to operate. At some later time, the cell voltage reaches zero and the cell is “run down.” Assume that the cell reaction is not limited by the mass of either electrode. (a) What will be the ratio of $[\text{Cd}^{2+}]$ to $[\text{Cu}^{2+}]$ when the cell is “run down”? (b) What will be their concentrations?
94. ▲ Repeat Exercise 93 for a standard zinc–nickel cell.
95. ▲ The cell potential for the cell $\text{Zn(s)} + 2\text{H}^+(\text{? M}) \longrightarrow \text{Zn}^{2+}(2.5 \text{ M}) + \text{H}_2(\text{g})$ (4.5 atm) is observed to be 0.445 V. What is the pH in the H^+/H_2 half-cell?
96. We wish to produce a 0.275-volt concentration cell using two hydrogen electrodes, both with hydrogen at a pressure of one atmosphere. One of the solutions has a pH of 1.5. Calculate the required pH of the other solution.
97. A concentration cell prepared using two hydrogen electrodes, both with the partial pressure of hydrogen being one atmosphere, produces 0.150 volts. The pH of one hydrogen electrode is 1.65; what is the pH of the other?

Relationships Among ΔG° , E°_{cell} , and K_{eq}

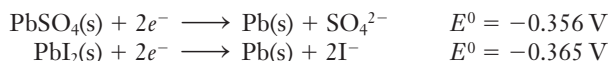
98. How are the signs and magnitudes of E°_{cell} , ΔG° , and K_{eq} related for a particular reaction? Why is the equilibrium constant K_{eq} related only to E°_{cell} and not to E_{cell} ?
99. In light of your answer to Exercise 98, how do you explain the fact that ΔG° for a redox reaction *does* depend on the number of electrons transferred, according to the equation $\Delta G^\circ = -nFE^\circ_{\text{cell}}$?
100. Calculate E°_{cell} from the tabulated standard reduction potentials for each of the following reactions in aqueous solution. Then calculate ΔG° and K_{eq} at 25°C from E°_{cell} . Which reactions are spontaneous as written?
- (a) $\text{MnO}_4^- + 5\text{Fe}^{2+} \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+}$ (acidic solution)
- (b) $2\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + \text{Cu(s)}$
- (c) $3\text{Zn(s)} + 2\text{MnO}_4^- + 4\text{H}_2\text{O} \longrightarrow 2\text{MnO}_2(\text{s}) + 3\text{Zn(OH)}_2(\text{s}) + 2\text{OH}^-$
101. Calculate ΔG° (overall) and ΔG° per mole of metal for each of the following reactions from E° values: (a) Zinc dissolves in dilute hydrochloric acid to produce a solution that contains Zn^{2+} , and hydrogen gas is evolved.

(b) Chromium dissolves in dilute hydrochloric acid to produce a solution that contains Cr^{3+} , and hydrogen gas is evolved. (c) Silver dissolves in dilute nitric acid to form a solution that contains Ag^+ , and NO is liberated as a gas. (d) Lead dissolves in dilute nitric acid to form a solution that contains Pb^{2+} , and NO is liberated as a gas.

102. For a certain cell, $\Delta G^\circ = 25.0 \text{ kJ}$. Calculate E° if n is (a) 1; (b) 2; (c) 4.
- Comment on the effect that the number of electrons exchanged has on the voltage of a cell.
103. Use tabulated reduction potentials to calculate the equilibrium constant for the reaction



104. Using the following half-reactions and E° data at 25°C:



calculate the equilibrium constant for the reaction



Practical Aspects of Electrochemistry

105. ● Distinguish among (a) primary voltaic cells, (b) secondary voltaic cells, and (c) fuel cells.
106. ● Sketch and describe the operation of (a) the Leclanché dry cell, (b) the lead storage battery, and (c) the hydrogen–oxygen fuel cell.
107. Why is the dry cell designed so that Zn and MnO_2 do not come into contact? What reaction might occur if they were in contact? How would this reaction affect the usefulness of the cell?



Charles D. Winters

108. ▲ People sometimes try to recharge dry cells, with limited success. (a) What reaction would you expect at the zinc electrode of a Leclanché cell in an attempt to recharge it? (b) What difficulties would arise from the attempt?
109. ● Briefly describe how a storage cell operates.
110. ● How does a fuel cell differ from a dry cell or a storage cell?
111. ● Does the physical size of a commercial cell govern the potential that it will deliver? What does the size affect?
112. Why is the electrode potential of the standard hydrogen electrode (SHE) 0.0000 volts?
113. What compound is produced by the chemical reaction that occurs in a hydrogen–oxygen fuel cell?
114. What commonly used metal forms a tough, transparent oxide surface layer that protects the metal from most

corrosive agents in the environment and, thus, inhibits corrosion?

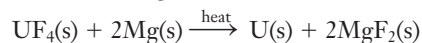
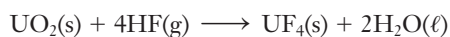
115. For a voltaic cell with the reaction



at what ratio of concentrations of lead and tin ions will $E_{\text{cell}} = 0$?

Mixed Exercises

116. Consider the electrochemical cell represented by $\text{Mg(s)} | \text{Mg}^{2+} || \text{Fe}^{3+} | \text{Fe(s)}$. (a) Write the half-reactions and the overall cell equation. (b) The standard reduction potential for $\text{Fe}^{3+}/\text{Fe(s)}$ is -0.036 V at 25°C . Determine the standard potential for the reaction. (c) Determine E for the cell when the concentration of Fe^{3+} is 10.0 mol/L and that of Mg^{2+} is $1.00 \times 10^{-3} \text{ mol/L}$. (d) If a current of 150 mA is to be drawn from this cell for a period of 20.0 min , what is the minimum mass change of the magnesium electrode?
117. A sample of Al_2O_3 dissolved in a molten fluoride bath is electrolyzed using a current of 1.20 A . (a) What is the rate of production of Al in g/h ? (b) The oxygen liberated at the positive carbon electrode reacts with the carbon to form CO_2 . What mass of CO_2 is produced per hour?
118. ▲ The “life” of a certain voltaic cell is limited by the amount of Cu^{2+} in solution available to be reduced. If the cell contains 30.0 mL of 0.165 M CuSO_4 , what is the maximum amount of electric charge this cell could generate?
119. A magnesium bar weighing 6.0 kg is attached to a buried iron pipe to protect the pipe from corrosion. An average current of 0.025 A flows between the bar and the pipe. (a) What reaction occurs at the surface of the bar? Of the pipe? In which direction do electrons flow? (b) How many years will be required for the Mg bar to be entirely consumed ($1 \text{ year} = 3.16 \times 10^7 \text{ s}$)? (c) What reaction(s) will occur if the bar is not replaced after the time calculated in (b)?
120. (a) Calculate the ratio of ion concentrations of Mn^{2+} and Fe^{2+} necessary to produce a voltaic cell of 1.45 volts . The electrodes are solid manganese and iron. (b) Draw this voltaic cell. Indicate which electrode is the anode and which is the cathode, as well as the direction of electron flow.
121. (a) Calculate the ratio of ion concentrations of Mg^{2+} and Cu^{2+} necessary to produce a voltaic cell of 2.69 volts . The electrodes are solid magnesium and solid copper. (b) Draw this voltaic cell. Indicate which electrode is the anode and which is the cathode, as well as the direction of electron flow.
122. The production of uranium metal from purified uranium dioxide ore consists of the following steps:



What is the oxidation number of U in (a) UO_2 , (b) UF_4 , and (c) U ? Identify (d) the reducing agent, and (e) the substance reduced. (f) What current could the second reaction produce if 0.500 g of UF_4 reacted each minute? (g) What volume of $\text{HF}(\text{g})$ at 25°C and 10.0 atm would be

required to produce 0.500 g of U ? (h) Would 0.500 g of Mg be enough to produce 0.500 g of U ?

123. Which of each pair is the stronger oxidizing agent? (a) H^+ or Cl_2 ; (b) Zn^{2+} or Se in contact with acidic solution; (c) $\text{Cr}_2\text{O}_7^{2-}$ or Br_2 (acidic solution)
124. (a) Describe the process of electroplating. (b) Sketch and label an apparatus that a jeweler might use for electroplating silver onto jewelry. (c) A jeweler purchases highly purified silver to use as the anode in an electroplating operation. Is this a wise purchase? Why?
125. The same quantity of electric charge that deposited 0.612 g of silver was passed through a solution of a gold salt, and 0.373 g of gold was deposited. What is the oxidation state of gold in this salt?

Conceptual Exercises

126. In the lead storage battery, what substance is produced at both the anode and the cathode during discharge?
127. What metals found in commonly used voltaic cells have presented environmental concerns due to their toxicity?
128. Both I_2 and Br_2 are commercially prepared by oxidation of their halide binary salts from oceans or natural waters, and Cl_2 can be prepared by electrolyzing aqueous NaCl solutions. Why then is it not possible to prepare F_2 by electrolysis of an aqueous NaF solution?
129. Electroplating is performed by using a source of direct current. (a) Why can't an alternating current be used? (b) What would happen if an alternating current were used for electroplating?
130. Figure 21-5 is a schematic diagram of the electrolytic cell used to separate copper from the impurities, that is, zinc, iron, silver, gold, and platinum. Can this process be used to separate the metals left after the copper has been removed? Explain.
131. ● A zinc-copper cell like that shown in Figure 21-6 is constructed, except that an inert platinum wire is used instead of the salt bridge. Will the cell still produce a potential?

Building Your Knowledge

132. An electrochemical cell was needed in which hydrogen and oxygen would react to form water. (a) Using the following standard reduction potentials for the couples given, determine which combination of half-reactions gives the maximum output potential:
 $E^0 = -0.828 \text{ V}$ for $\text{H}_2\text{O}(\ell)/\text{H}_2(\text{g}), \text{OH}^-$
 $E^0 = 0.0000 \text{ V}$ for $\text{H}^+/\text{H}_2(\text{g})$
 $E^0 = 1.229 \text{ V}$ for $\text{O}_2(\text{g}), \text{H}^+/\text{H}_2\text{O}(\ell)$
 $E^0 = 0.401 \text{ V}$ for $\text{O}_2(\text{g}), \text{H}_2\text{O}(\ell)/\text{OH}^-$
 (b) Write the balanced equation for the overall reaction in (a).
133. (a) Given the following E^0 values at 25°C , calculate K_{sp} for cadmium sulfide, CdS .
 $\text{Cd}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Cd(s)} \quad E^0 = -0.403 \text{ V}$
 $\text{CdS(s)} + 2e^- \longrightarrow \text{Cd(s)} + \text{S}^{2-}(\text{aq}) \quad E^0 = -1.21 \text{ V}$
 (b) Evaluate ΔG^0 at 25°C for the process



Molecular Reasoning exercises



More Challenging exercises

Blue-Numbered

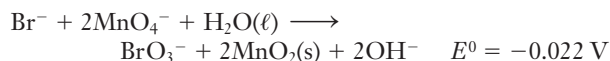
exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

134. Refer to tabulated reduction potentials. (a) Calculate K_{sp} for AgBr(s) . (b) Calculate ΔG^0 for the reaction

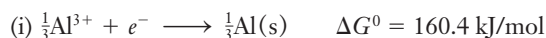


135. ▲ Under standard-state conditions, the following reaction is not spontaneous:

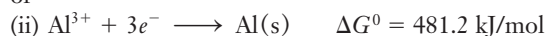


The reaction conditions are adjusted so that $E = 0.120 \text{ V}$ by making $[\text{Br}^-] = [\text{MnO}_4^-] = 1.60 \text{ mol/L}$ and $[\text{BrO}_3^-] = 0.60 \text{ mol/L}$. (a) What is the concentration of hydroxide ions in this cell? (b) What is the pH of the solution in the cell?

136. Show by calculation that $E^0 = -1.662 \text{ V}$ for the reduction of Al^{3+} to Al(s) , regardless of whether the equation for the reaction is written



or



137. We wish to fill a balloon with H_2 at a pressure of 1.10 atm and a temperature of 25°C . The volume of the balloon when filled is 750 mL. How long must a current of 2.75 A be passed through the cell in order to produce this amount of H_2 by electrolysis of water?
138. In the electrolysis of water with copper electrodes (or with most other common metals), the amount of $\text{O}_2(\text{g})$ produced is less than when one uses Pt electrodes. The amount of H_2 produced is the same for either electrode material. Explain.

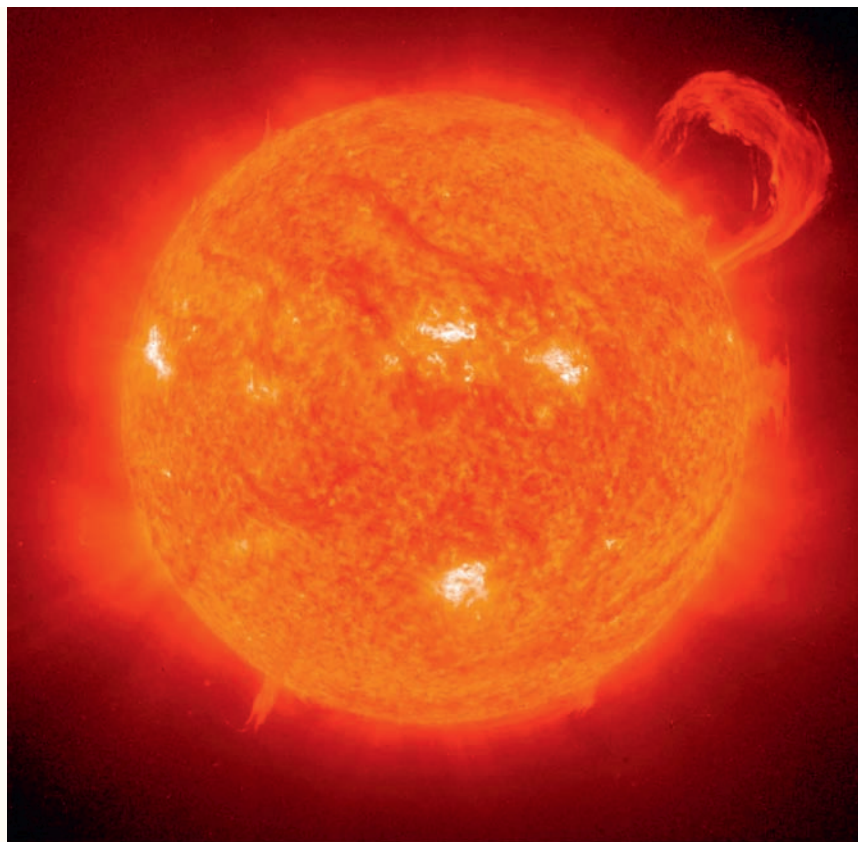
Beyond the Textbook

NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.*

139. Search the web to locate information on ion-selective electrodes. List five applications of ion-selective electrodes.
140. Use a reference book or search the web to locate a table of reduction potentials. List five half-reactions that are not in Appendix J and give the reduction potential of each.
141. Search the web to locate information on micro pH probes. The smallest probes that you found information about required an immersion depth of approximately how many millimeters?
142. Farrah Day's Beauty Salon advertises the removal of unwanted hair by "galvanic electrolysis." In this technique, a power supply is used to apply electrical current to the hair follicle using a tiny probe (electrode), generating tissue-destroying lye (NaOH) from body moisture and salts. (a) What's wrong with the name "galvanic electrolysis"? (b) Can you more accurately name the type of electrolytic cell involved? (c) What cell discussed in this chapter describes the electrochemical reactions taking place? Calculate the E^0_{cell} for the process.

Nuclear Chemistry

22



Our sun supplies energy to the earth from a distance of 93,000,000 miles. Like other stars, it is a giant nuclear fusion reactor. Much of its energy comes from the fusion of deuterium, ${}^2_1\text{H}$, producing helium, ${}^4_2\text{He}$.

NASA

OUTLINE

- 22-1** The Nucleus
- 22-2** Neutron–Proton Ratio and Nuclear Stability
- 22-3** Nuclear Stability and Binding Energy
- 22-4** Radioactive Decay
- 22-5** Equations for Nuclear Reactions
- 22-6** Neutron-Rich Nuclei (Above the Band of Stability)
- 22-7** Neutron-Poor Nuclei (Below the Band of Stability)
- 22-8** Nuclei with Atomic Number Greater Than 83
- 22-9** Detection of Radiation
- 22-10** Rates of Decay and Half-Life
- 22-11** Decay Series
- 22-12** Uses of Radionuclides
- 22-13** Artificial Transmutations of Elements
- 22-14** Nuclear Fission
- 22-15** Nuclear Fission Reactors
- 22-16** Nuclear Fusion

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Describe the makeup of the nucleus
- ▶ Describe the relationships between neutron–proton ratio and nuclear stability
- ▶ Tell what is meant by the band of stability
- ▶ Calculate mass deficiency and nuclear binding energy
- ▶ Describe the common types of radiation emitted when nuclei undergo radioactive decay
- ▶ Write and balance equations that describe nuclear reactions
- ▶ Predict the different kinds of nuclear reactions and describe how these reactions depend on positions of the nuclei relative to the band of stability
- ▶ Describe methods for detecting radiation
- ▶ Understand half-lives of radioactive elements
- ▶ Carry out calculations associated with radioactive decay
- ▶ Interpret decay series
- ▶ Tell about some uses of radionuclides, including the use of radioactive elements for dating objects
- ▶ Describe some nuclear reactions that are induced by bombardment of nuclei with particles
- ▶ Tell about nuclear fission and some of its applications, including nuclear reactors
- ▶ Tell about nuclear fusion and some prospects for and barriers to its use for the production of energy

Chemical properties are determined by electron distributions and are only indirectly influenced by atomic nuclei. Until now, we have discussed ordinary chemical reactions, so we have focused on electron configurations. **Nuclear reactions** involve changes in the composition of nuclei. These extraordinary processes are often accompanied by the release of tremendous amounts of energy and by transmutations of elements. Some differences between nuclear reactions and ordinary chemical reactions follow.

Nuclear Reaction	Chemical Reaction
1. Elements may be converted from one to another.	1. No new elements can be produced.
2. Particles within the nucleus are involved.	2. Only the electrons participate.
3. Tremendous amounts of energy are released or absorbed.	3. Relatively small amounts of energy are released or absorbed.
4. Rate of reaction is not influenced by external factors.	4. Rate of reaction depends on factors such as concentration, temperature, catalyst, and pressure.

Medieval alchemists spent lifetimes trying to convert other metals into gold without success. Years of failure and the acceptance of Dalton's atomic theory early in the 19th century convinced scientists that one element could not be converted into another. Then, in 1896, Henri Becquerel discovered "radioactive rays" (*natural radioactivity*) coming from a uranium compound. Ernest Rutherford's study of these rays showed that atoms of one element may indeed be converted into atoms of other elements by spontaneous nuclear disintegrations. Many years later, it was shown that nuclear reactions initiated by bombardment of nuclei with accelerated subatomic particles or other nuclei can also transform one element into another—accompanied by the release of radiation (*induced radioactivity*).

Becquerel's discovery led other researchers, including Marie and Pierre Curie, to discover and study new radioactive elements. Many radioactive isotopes, or **radioisotopes**, now have important medical, agricultural, and industrial uses.

Nuclear fission is the splitting of a heavy nucleus into lighter nuclei. **Nuclear fusion** is the combination of light nuclei to produce a heavier nucleus. These processes release huge amounts of energy that could satisfy a large portion of our future energy demands. Current research is aimed at surmounting the technological problems associated with safe and efficient use of nuclear fission reactors and with the development of controlled fusion reactors.

▶ In Chapter 4, we represented an atom of a particular isotope by its *nuclide symbol*. Radioisotopes are often called **radionuclides**.

Table 22-1 Fundamental Particles of Matter

Particle	Mass	Charge
Electron (e^-)	0.00054858 amu	1−
Proton (p or p^+)	1.0073 amu	1+
Neutron (n or n^0)	1.0087 amu	none

22-1 The Nucleus

In Chapter 4, we described the principal subatomic particles (Table 22-1). Recall that the neutrons and protons together constitute the nucleus, with the electrons occupying essentially empty space around the nucleus. The nucleus is only a minute fraction of the total volume of an atom; yet nearly all the mass of an atom resides in the nucleus. Thus, nuclei are extremely dense. It has been shown experimentally that nuclei of all elements have approximately the same density, $2.4 \times 10^{14} \text{ g/cm}^3$.

From an electrostatic point of view, it is amazing that positively charged protons can be packed so closely together. Yet many nuclei do not spontaneously decompose, so they must be stable. When Rutherford postulated the nuclear model of the atom in the early 20th century, scientists were puzzled by such a situation. Physicists have since detected many very short-lived subatomic particles (in addition to protons, neutrons, and electrons) as products of nuclear reactions. Well over 100 have been identified. A discussion of most of these particles is beyond the scope of a chemistry text. Furthermore, their functions are not entirely understood, but it is now thought that they help to overcome the proton-proton repulsions and to bind nuclear particles (**nucleons**) together. The attractive forces among nucleons appear to be important over only extremely small distances, about 10^{-13} cm .



AP/Nichols Bohr Library

Marie Skłodowska-Curie (1867–1934) is the only person to have been honored with Nobel Prizes in both physics and chemistry. In 1903, Pierre (1859–1906) and Marie Curie and Henri Becquerel (1852–1908) shared the prize in physics for the discovery of natural radioactivity. Marie Curie also received the 1911 Nobel Prize in Chemistry for her discovery of radium and polonium and the compounds of radium. She named polonium for her native Poland. Marie's daughter, Irene Joliot-Curie (1897–1956), and Irene's husband, Frederick Joliot (1900–1958), received the 1935 Nobel Prize in Chemistry for the first synthesis of a new radioactive element.

22-2 Neutron-Proton Ratio and Nuclear Stability

The term “**nuclide**” is used to refer to different atomic forms of all elements. The term “isotope” applies only to different forms of the same element. Most naturally occurring nuclides have even numbers of protons and even numbers of neutrons; 157 nuclides fall into this category. Nuclides with odd numbers of both protons and neutrons are least common (there are only four), and those with odd-even and even-odd combinations are intermediate in abundance (Table 22-2). Furthermore, nuclides with certain “magic numbers” of protons and neutrons seem to be especially stable. Nuclides with a number of protons *or* a number of neutrons *or* a sum of the two equal to 2, 8, 20, 28, 50, 82, or 126 have unusual stability. Examples are ${}^4_2\text{He}$, ${}^{16}_8\text{O}$, ${}^{42}_{20}\text{Ca}$, ${}^{88}_{38}\text{Sr}$, and ${}^{208}_{82}\text{Pb}$. This suggests an energy level (shell) model for the nucleus analogous to the shell model of electron configurations.

Figure 22-1 is a plot of the number of neutrons (N) versus number of protons (Z) for the nuclides. For low atomic numbers, the most stable nuclides have equal numbers of protons and neutrons ($N = Z$). Above atomic number 20, the most stable nuclides have more neutrons than protons. Careful examination reveals an approximately stepwise shape to the plot due to the stability of nuclides with even numbers of nucleons.

► If enough nuclei could be gathered together to occupy one cubic centimeter, the total weight would be about 250 million tons!

► The nuclide symbol for an element (Section 4-7) is

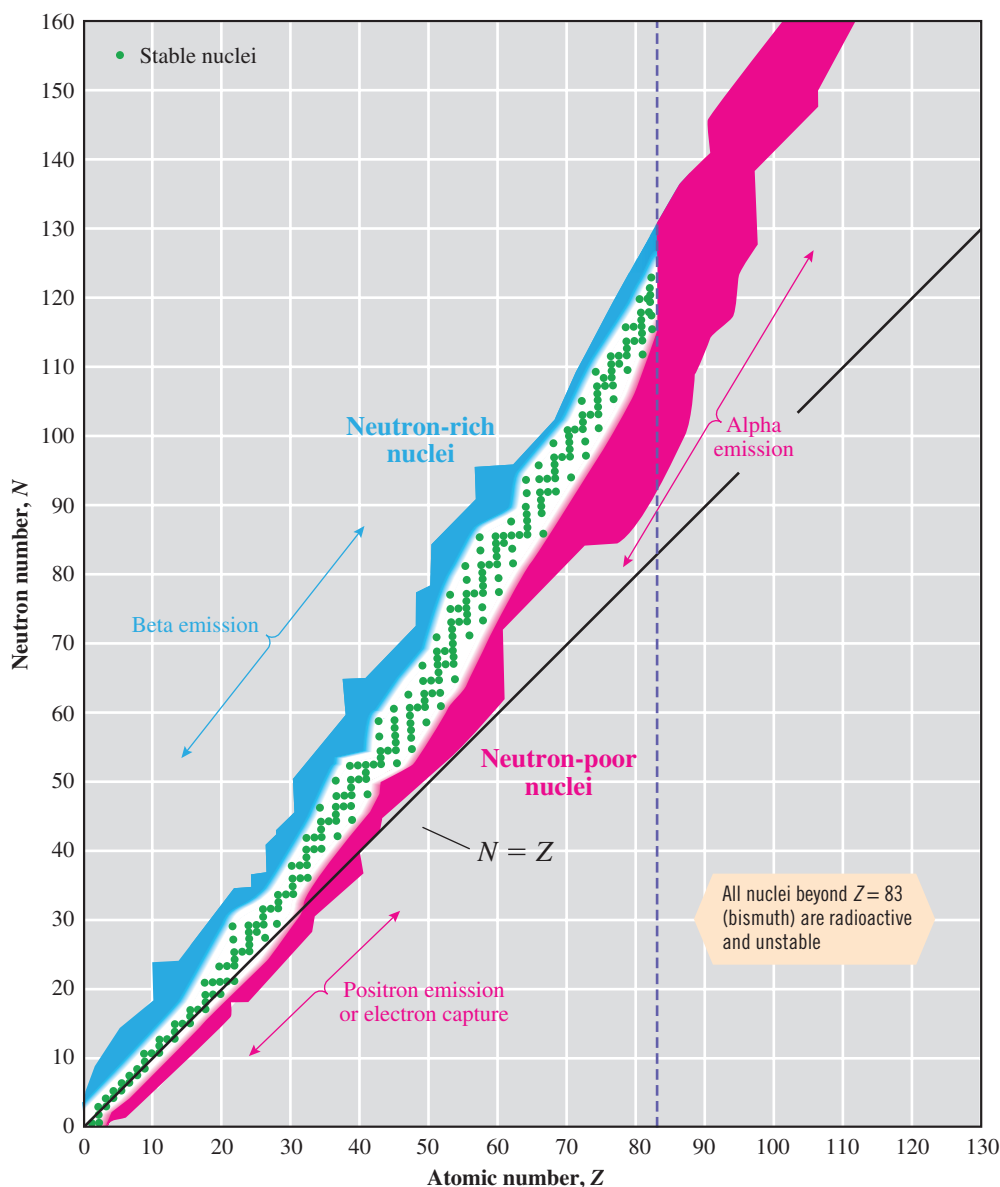
$${}^A_Z E$$

where E is the chemical symbol for the element, Z is its atomic number, and A is its mass number.

Table 22-2 Abundance of Naturally Occurring Nuclides

Number of protons	even	even	odd	odd
Number of neutrons	even	odd	even	odd
Number of such nuclides	157	52	50	4

Figure 22-1 A plot of the number of neutrons, N , versus the number of protons, Z , in nuclei. The stable nuclei (green dots) are located in an area known as the **band of stability**. All other nuclei in the white, pink, and blue regions are unstable and radioactive. No nuclei exist in the large gray shaded region. Most unstable, radioactive nuclei occur outside the band of stability. As atomic number increases, the N/Z ratio of the stable nuclei increases. Unstable nuclei above the band of stability are referred to as neutron-rich nuclei (blue shading); those below the band of stability are called neutron-poor nuclei (pink shading). Unstable (radioactive) nuclei decay by alpha emission, beta emission, positron emission, or electron capture. Lighter neutron-poor nuclei usually decay by positron emission or electron capture, either of which converts a proton into a neutron. Heavier neutron-poor nuclei usually decay by alpha emission, which decreases the neutron/proton ratio. Neutron-rich nuclei decay by beta emission, which transforms a neutron into a proton. Decay by alpha emission is by far the most predominant mode of decay for nuclei with atomic numbers beyond 83 (bismuth).



22-3 Nuclear Stability and Binding Energy

Experimentally, we observe that the masses of atoms other than ^1_1H are always *less* than the sum of the masses of their constituent particles. We can now explain why this *mass deficiency* occurs. We also now know that the mass deficiency is in the nucleus of the atom and has nothing to do with the electrons; however, *because tables of masses of isotopes include the electrons, we shall also include them.*

The **mass deficiency**, Δm , for a nucleus is the difference between the sum of the masses of electrons, protons, and neutrons in the atom (the calculated mass) and the actual measured mass of the atom.

$$\Delta m = (\text{sum of masses of all } e^-, p^+, \text{ and } n^0) - (\text{actual mass of atom})$$

For most naturally occurring isotopes, the mass deficiency is only about 0.15% or less of the calculated mass of an atom.

► Be sure you know how to find the numbers of protons, neutrons, and electrons in a specified atom. Review Section 4-7.

EXAMPLE 22-1 Mass Deficiency

Calculate the mass deficiency for chlorine-35 atoms in amu/atom and in g/mol atoms. The actual mass of a chlorine-35 atom is 34.9689 amu.

Plan

We first find the numbers of protons, electrons, and neutrons in one atom. Then we determine the “calculated” mass as the sum of the masses of these particles. The mass deficiency is the actual mass subtracted from the calculated mass. This deficiency is commonly expressed either as mass per atom or as mass per mole of atoms.

Solution

Each atom of $^{35}_{17}\text{Cl}$ contains 17 protons, 17 electrons, and $(35 - 17) = 18$ neutrons. First we sum the masses of these particles.

$$\begin{array}{llll} \text{protons:} & 17 \times 1.0073 \text{ amu} & = & 17.124 \text{ amu} & \text{(masses from Table 22-1)} \\ \text{electrons:} & 17 \times 0.00054858 \text{ amu} & = & 0.0093 \text{ amu} \\ \text{neutrons:} & 18 \times 1.0087 \text{ amu} & = & 18.157 \text{ amu} \\ \hline & \text{sum} & = & 35.290 \text{ amu} & \leftarrow \text{calculated mass} \end{array}$$

Then we subtract the actual mass from the “calculated” mass to obtain Δm .

$$\Delta m = 35.290 \text{ amu} - 34.9689 \text{ amu} = 0.321 \text{ amu} \quad \text{mass deficiency (in one atom)}$$

We have calculated the mass deficiency in amu/atom. Recall (Section 4-9) that 1 gram is equal to 6.022×10^{23} amu. We can show that a number expressed in amu/atom is equal to the same number in g/mol of atoms:

$$\begin{aligned} \frac{\text{g}}{\text{mol}} &= \frac{0.321 \text{ amu}}{\text{atom}} \times \frac{1 \text{ g}}{6.022 \times 10^{23} \text{ amu}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol } ^{35}\text{Cl atoms}} \\ &= 0.321 \text{ g/mol of } ^{35}\text{Cl atoms} \quad \leftarrow \text{(mass deficiency in a mole of Cl atoms)} \end{aligned}$$

You should now work Exercises 14a and 16a, b.

What has happened to the mass represented by the mass deficiency? In 1905, Einstein set forth the Theory of Relativity, which stated that matter and energy are equivalent. An obvious corollary is that matter can be transformed into energy and energy into matter. The transformation of matter into energy occurs in the sun and other stars. It happened on earth when controlled nuclear fission was achieved in 1939 (Section 22-14). The reverse transformation, energy into matter, has not yet been accomplished on a large scale. Einstein’s equation, which we encountered in Chapter 1, is $E = mc^2$. E represents the amount of energy released, m the mass of matter transformed into energy, and c the speed of light in a vacuum, 2.997925×10^8 m/s (usually rounded off to 3.00×10^8 m/s).

A mass deficiency represents the amount of matter that would be converted into energy and released if the nucleus were formed from initially separate protons and neutrons. This energy is the **nuclear binding energy (BE)**. It provides the powerful short-range force that holds the nuclear particles (protons and neutrons) together in a very small volume.

We can rewrite the Einstein relationship as

$$BE = (\Delta m)c^2$$

Specifically, if 1 mole of ^{35}Cl nuclei were to be formed from 17 moles of protons and 18 moles of neutrons, the resulting mole of nuclei would weigh 0.321 gram less than the original collection of protons and neutrons (Example 22-1).

Nuclear binding energies may be expressed in many different units, including kilojoules/mole of atoms, kilojoules/gram of atoms, and megaelectron volts/nucleon. Some useful equivalences are

► The abbreviation “M” stands for the prefix “mega,” meaning 10^6 or “million” (Table 1-6).

$$\begin{aligned} 1 \text{ megaelectron volt (MeV)} &= 1 \text{ million electron volts} = 1.60 \times 10^{-13} \text{ J} \\ 1 \text{ joule (J)} &= 1 \text{ kg} \cdot \text{m}^2/\text{s}^2 \end{aligned}$$

Let’s use the value of Δm for ^{35}Cl to calculate its nuclear binding energy.

EXAMPLE 22-2 Nuclear Binding Energy

Calculate the nuclear binding energy of ^{35}Cl in (a) kilojoules per mole of Cl atoms, (b) kilojoules per gram of Cl atoms, and (c) megaelectron volts per nucleon.

Plan

The mass deficiency that we calculated in Example 22-1 is related to the binding energy by the Einstein equation.

Solution

The mass deficiency is $0.321 \text{ g/mol} = 3.21 \times 10^{-4} \text{ kg/mol}$.

$$\begin{aligned} \text{(a)} \quad BE &= (\Delta m)c^2 = \frac{3.21 \times 10^{-4} \text{ kg}}{\text{mol } ^{35}\text{Cl atoms}} \times (3.00 \times 10^8 \text{ m/s})^2 = 2.89 \times 10^{13} \frac{\text{kg} \cdot \text{m}^2/\text{s}^2}{\text{mol } ^{35}\text{Cl atoms}} \\ &= 2.89 \times 10^{13} \text{ J/mol } ^{35}\text{Cl atoms} = 2.89 \times 10^{10} \text{ kJ/mol of } ^{35}\text{Cl atoms} \end{aligned}$$

(b) From Example 22-1, the actual mass of ^{35}Cl is

$$\frac{34.9689 \text{ amu}}{^{35}\text{Cl atom}} \quad \text{or} \quad \frac{34.9689 \text{ g}}{\text{mol } ^{35}\text{Cl atoms}}$$

We use this mass to set up the needed conversion factor.

$$BE = \frac{2.89 \times 10^{10} \text{ kJ}}{\text{mol of } ^{35}\text{Cl atoms}} \times \frac{1 \text{ mol } ^{35}\text{Cl atoms}}{34.9689 \text{ g } ^{35}\text{Cl atoms}} = 8.26 \times 10^8 \text{ kJ/g } ^{35}\text{Cl atoms}$$

(c) The number of nucleons in *one* atom of ^{35}Cl is 17 protons + 18 neutrons = 35 nucleons.

$$\begin{aligned} BE &= \frac{2.89 \times 10^{10} \text{ kJ}}{\text{mol of } ^{35}\text{Cl atoms}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1 \text{ MeV}}{1.60 \times 10^{-13} \text{ J}} \times \frac{1 \text{ mol } ^{35}\text{Cl atoms}}{6.022 \times 10^{23} \text{ } ^{35}\text{Cl atoms}} \times \frac{1 \text{ } ^{35}\text{Cl atom}}{35 \text{ nucleons}} \\ &= 8.57 \text{ MeV/nucleon} \end{aligned}$$

You should now work Exercises 14 and 16.

► The mass number, A , is equal to the number of nucleons in one atom (see Section 4-7).

► Some unstable radioactive nuclei do emit a single proton, a single neutron, or other subatomic particles as they decay in the direction of greater stability. None decomposes entirely into elementary particles.

The nuclear binding energy of a mole of ^{35}Cl nuclei, $2.89 \times 10^{13} \text{ J/mol}$, is an enormous amount of energy—enough to heat $6.9 \times 10^7 \text{ kg}$ ($\approx 76,000$ tons) of water from 0°C to 100°C ! Stated differently, this is also the amount of energy that would be required to separate 1 mole of ^{35}Cl nuclei into 17 moles of protons and 18 moles of neutrons. This has never been done.

Figure 22-2 is a plot of average binding energy per gram of nuclei versus mass number. It shows that nuclear binding energies (per gram) increase rapidly with increasing mass number, reach a maximum around mass number 50, and then decrease slowly. The nuclei with the highest binding energies (mass numbers 40 to 150) are the most stable. Large amounts of energy would be required to separate these nuclei into their component neu-

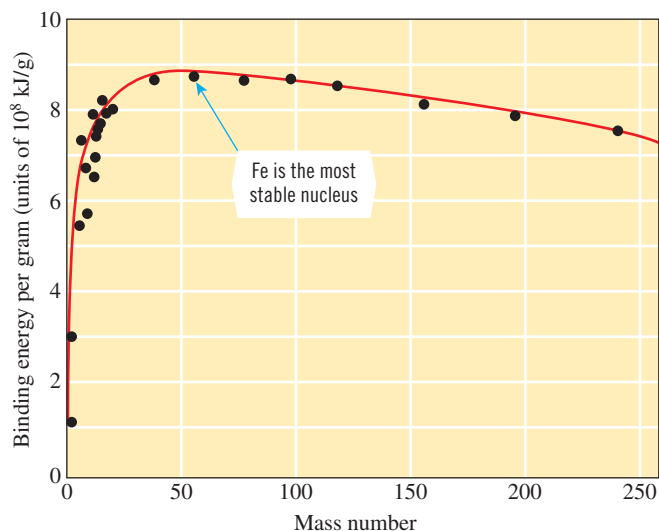


Figure 22-2 Plot of binding energy per gram versus mass number. Very light and very heavy nuclei are relatively unstable.

trons and protons. Even though these nuclei are the most stable ones, *all* nuclei are stable with respect to complete decomposition into protons and neutrons because all (except ^1H) nuclei have mass deficiencies. In other words, the energy equivalent of the loss of mass represents an associative force that is present in all nuclei except ^1H . It must be overcome to separate the nuclei completely into their subatomic particles.

22-4 Radioactive Decay

Nuclei whose neutron-to-proton ratios lie outside the stable region undergo spontaneous radioactive decay by emitting one or more particles or electromagnetic rays or both. The type of decay that occurs usually depends on whether the nucleus is above, below, or to the right of the band of stability (see Figure 22-1). Common types of **radiation** emitted in decay processes are summarized in Table 22-3.

The particles can be emitted at different kinetic energies. In addition, radioactive decay often leaves a nucleus in an excited (high-energy) state. Then the decay is followed by gamma ray emission.



The energy of the **gamma ray** ($h\nu$) is equal to the energy difference between the ground and excited nuclear states. This is like the emission of lower-energy electromagnetic radiation that occurs as an atom in its excited electronic state returns to its ground state (see Section 4-13). Studies of gamma-ray energies strongly suggest that nuclear energy levels are quantized just as are electronic energy levels. This adds further support for a shell model for the nucleus.

The penetrating abilities of the particles and rays are proportional to their energies. Beta particles and positrons are about 100 times more penetrating than the heavier and slower-moving alpha particles. They can be stopped by a $\frac{1}{8}$ -inch-thick (0.3 cm) aluminum plate. They can burn skin severely but cannot reach internal organs. Alpha particles have low penetrating ability and cannot damage or penetrate skin. They can damage sensitive internal tissue if inhaled, however. The high-energy gamma rays have great penetrating power and severely damage both skin and internal organs. They travel at the speed of light and can be stopped by thick layers of concrete or lead.

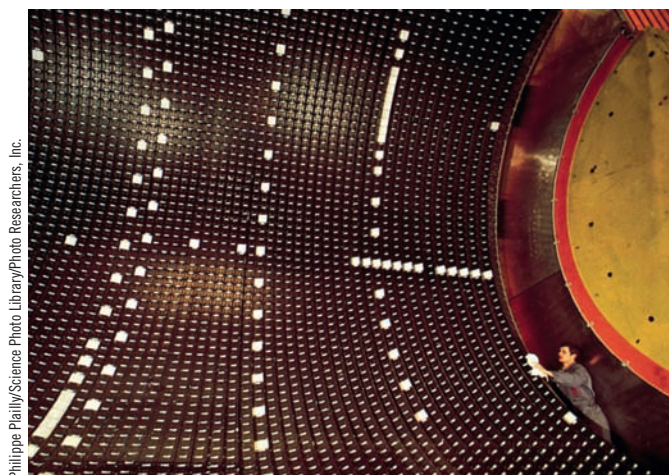
► Recall that the energy of electromagnetic radiation is $E = h\nu$, where h is Planck's constant and ν is the frequency.

Table 22-3 Common Types of Radioactive Emissions

Type and Symbol ^a	Identity	Mass (amu)	Charge	Velocity	Penetration
beta (β , β^- , ${}^0_{-1}\beta$, ${}^0_{-1}e$)	electron	0.00055	1−	≤90% speed of light	low to moderate, depending on energy
positron ^b (${}^0_{+1}\beta$, ${}^0_{+1}e$)	positively charged electron	0.00055	1+	≤90% speed of light	low to moderate, depending on energy
alpha (α , ${}^4_2\alpha$, ${}^4_2\text{He}$)	helium nucleus	4.0026	2+	≤10% speed of light	low
proton (1_1p , ${}^1_1\text{H}$)	proton, hydrogen nucleus	1.0073	1+	≤10% speed of light	low to moderate, depending on energy
neutron (0_1n)	neutron	1.0087	0	≤10% speed of light	very high
gamma (${}^0_0\gamma$) ray	high-energy electromagnetic radiation such as X-rays	0	0	speed of light	high

^aThe number at the upper left of the symbol is the number of nucleons, and the number at the lower left is the number of positive charges.

^bOn the average, a positron exists for about a nanosecond (1×10^{-9} second) before colliding with an electron and being converted into the corresponding amount of energy.



Philippe Plailly/Science Photo Library/Photo Researchers, Inc.

A technician cleans lead glass blocks that form part of the giant OPAL particle detector at CERN, the European center for particle physics near Geneva, Switzerland.



Will and Doni McIntyre/Photo Researchers, Inc.

Robotics technology is used to manipulate highly radioactive samples safely.

22-5 Equations for Nuclear Reactions

In *chemical* reactions, atoms in molecules and ions are rearranged, but matter is neither created nor destroyed, and atoms are not changed into other atoms. In earlier chapters, we learned to write balanced chemical equations to represent chemical reactions. Such equations must show the same total number of atoms of each kind on both sides of the equation and the same total charge on both sides of the equation. In a nuclear reaction, a different kind of transformation occurs, one in which a proton can change into a neutron, a neutron can change into a proton, or particles can be captured by or ejected from the nucleus, but the total number of nucleons remains the same. This leads to two requirements for the equation for a nuclear reaction:

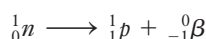
1. The sum of the mass numbers (the left superscript in the nuclide symbol) of the reactants must equal the sum of the mass numbers of the products; this maintains mass balance.

2. The sum of the atomic numbers (the left subscript in the nuclide symbol) of the reactants must equal the sum of the atomic numbers of the products; this maintains charge balance.

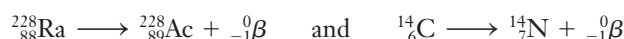
Because such equations are intended to describe only the changes in the nucleus, they do not ordinarily include ionic charges (which are due to changes in the arrangements of electrons). In the following sections, we will see many examples of such equations for nuclear reactions. For several of these, the check for mass balance and charge balance is illustrated in the margin.

22-6 Neutron-Rich Nuclei (Above the Band of Stability)

Nuclei in this region have too high a ratio of neutrons to protons. They undergo decays that *decrease* the ratio. The most common such decay is **beta emission**. A **beta particle** is an electron ejected *from the nucleus* when a neutron is converted into a proton.



Thus, beta emission results in an increase of one in the number of protons (the atomic number) and a decrease of one in the number of neutrons, with no change in mass number. Examples of beta-particle emission are



The sum of the mass numbers on each side of the first equation is 228, and the sum of the atomic numbers on each side is 88. The corresponding sums for the second equation are 14 and 6, respectively.

► For beta emission by ${}_{88}^{228}\text{Ra}$:

mass balance (superscripts):

$$228 \longrightarrow 228 + 0$$

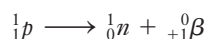
charge balance (subscripts):

$$88 \longrightarrow 89 + (-1) = 88$$

22-7 Neutron-Poor Nuclei (Below the Band of Stability)

Two types of decay for nuclei below the band of stability are **positron emission** or **electron capture** (*K* capture). Positron emission is most commonly encountered with artificially radioactive nuclei of the lighter elements. Electron capture occurs most often with heavier elements.

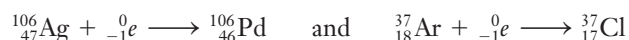
A **positron** has the mass of an electron, but a positive charge. Positrons are emitted when protons are converted to neutrons.



Thus, positron emission results in a *decrease* by one in atomic number and an *increase* by one in the number of neutrons, with *no change* in mass number.



The same effect can be accomplished by electron capture (*K* capture), in which an electron from the *K* shell ($n = 1$) is captured by the nucleus. This is very different from an atom gaining an electron to form an ion.



Some nuclides, such as ${}_{11}^{22}\text{Na}$, undergo both electron capture and positron emission.



Some of the neutron-poor nuclei, especially the heavier ones, *increase* their neutron-to-proton ratios by undergoing **alpha emission**. **Alpha particles** are helium nuclei, ${}_2^4\text{He}$, consisting of two protons and two neutrons. Alpha particles carry a double positive charge,

► For positron emission by ${}_{19}^{38}\text{K}$:

$$\text{mass: } 38 \longrightarrow 38 + 0$$

$$\text{charge: } 19 \longrightarrow 18 + 1 = 19$$

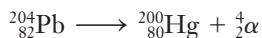
► For electron capture by ${}_{18}^{37}\text{Ar}$:

$$\text{mass: } 37 + 0 \longrightarrow 37$$

$$\text{charge: } 18 + (-1) \longrightarrow 17$$

► For α -emission by $^{204}_{82}\text{Pb}$:
 mass: $204 \longrightarrow 200 + 4 = 204$
 charge: $82 \longrightarrow 80 + 2 = 82$

but charge is usually not shown in nuclear reactions. Alpha emission also results in an increase of the neutron-to-proton ratio. An example is the alpha emission of lead-204.



22-8 Nuclei with Atomic Number Greater Than 83

► The only stable nuclide with atomic number 83 is $^{209}_{83}\text{Bi}$.

All nuclides with atomic number greater than 83 are beyond the band of stability and are radioactive. Many of these decay by alpha emission.



The decay of radium-226 was originally reported in 1902 by Rutherford and Soddy. It was the first transmutation of an element ever observed. A few heavy nuclides also decay by beta emission, positron emission, and electron capture.

Some isotopes of uranium ($Z = 92$) and elements of higher atomic number, the **transuranium elements**, also decay by spontaneous nuclear fission. In this process, a heavy nuclide splits to form nuclides of intermediate mass and emits neutrons.

► For fission of $^{252}_{98}\text{Cf}$:
 mass: $252 \longrightarrow 142 + 106 + 4(1) = 252$
 charge: $98 \longrightarrow 56 + 42 + 4(0) = 98$



EXAMPLE 22-3 Equations for Nuclear Decay Reactions

Write the balanced equation for each of the following radioactive decay processes.

- ^{45}Ti decays by positron emission.
- ^{81}Kr decays by electron capture.
- ^{104}Ru decays by beta emission.
- ^{223}Ra decays by alpha emission.

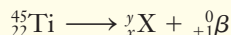
Plan

For each process, write the nuclide symbols for the reactant species and for the particle that is captured (as a reactant) or that is emitted (as a product). Then use mass balance and charge balance to write the super- and subscripts for the product nuclide. Determine the atomic symbol for the product nuclide from its atomic number (the subscript).

Solution

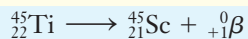
Represent the unknown product nuclide as ^y_xX .

- (a) Ti (atomic number 22) emits a positron ($^0_{+1}\beta$ or $^0_{+1}e$)

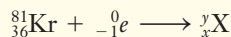


$$\begin{array}{lcl} \text{mass balance:} & 45 = y + 0; y = 45 \\ \text{charge balance:} & 22 = x + 1; x = 21 \end{array} \Bigg\} \Rightarrow ^{45}_{21}\text{X}$$

The element with atomic number 21 is scandium, Sc, so the complete equation is

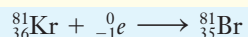


- (b) Kr (atomic number 36) captures an electron ($^0_{-1}e$)

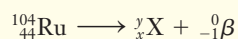


$$\begin{array}{lcl} \text{mass balance:} & 81 + 0 = y; y = 81 \\ \text{charge balance:} & 36 - 1 = x; x = 35 \end{array} \Bigg\} \Rightarrow ^{81}_{35}\text{X}$$

The element with atomic number 35 is bromine, Br, so the complete equation is

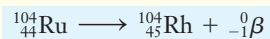


(c) Ru (atomic number 44) emits a beta particle (${}^0_{-1}\beta$ or ${}^0_{-1}e$)

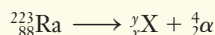


$$\begin{array}{lcl} \text{mass balance:} & 104 = y + 0; y = 104 & \\ \text{charge balance:} & 44 = x - 1; x = 45 & \end{array} \Bigg\} \Rightarrow {}^{104}_{45}\text{X}$$

The element with atomic number 45 is rhodium, Rh, so the complete equation is

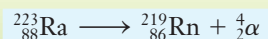


(d) Ra (atomic number 88) emits an alpha particle (${}^4_2\alpha$)



$$\begin{array}{lcl} \text{mass balance:} & 223 = y + 4; y = 219 & \\ \text{charge balance:} & 88 = x + 2; x = 86 & \end{array} \Bigg\} \Rightarrow {}^{219}_{86}\text{X}$$

The element with atomic number 86 is radon, Rn, so the complete equation is



You should now work Exercises 34 and 35.

22-9 Detection of Radiation

Photographic Detection

Emanations from radioactive substances affect photographic plates just as ordinary visible light does. Becquerel's discovery of radioactivity resulted from the unexpected exposure of such a plate, wrapped in black paper, by a nearby enclosed sample of a uranium-containing compound, potassium uranyl sulfate. After a photographic plate has been developed and fixed, the intensity of the exposed area is related to the amount of radiation that has struck the plate. Quantitative detection of radiation by this method is difficult and tedious.

Detection by Fluorescence

Fluorescent substances can absorb high-energy radiation such as gamma rays and subsequently emit visible light. As the radiation is absorbed, the absorbing atoms jump to excited electronic states. The excited electrons return to their ground states through a series of transitions, some of which emit visible light. This method may be used for the quantitative detection of radiation, using an instrument called a **scintillation counter**.

Cloud Chambers

The original cloud chamber was devised by C. T. R. Wilson (1869–1959) in 1911. A chamber contains air saturated with vapor. Particles emitted from a radioactive substance ionize air molecules in the chamber. Cooling the chamber causes droplets of liquid to condense on these ions. The paths of the particles can be followed by observing the fog-like tracks produced. The tracks may be photographed and studied in detail. Figures 22-3 and 22-4 show a cloud chamber and a cloud chamber photograph, respectively.

Unless otherwise noted, all content on this page is © Cengage Learning.

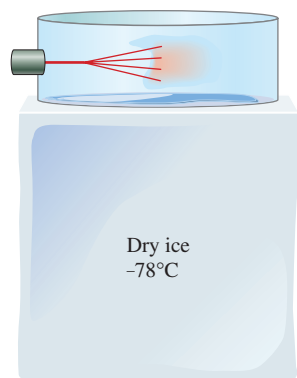


Figure 22-3 A cloud chamber. The emitter is glued onto a pin stuck into a stopper that is mounted on the chamber wall. The chamber has some volatile liquid in the bottom and rests on dry ice. The cool air near the bottom becomes supersaturated with vapor. When an emission speeds through this vapor, ions are produced. These ions serve as sites about which the vapor condenses, forming tiny droplets, or fog.

Science Source/Photo Researchers



Figure 22-4 Colored image obtained from a bubble chamber (a modern version of the cloud chamber) at the Stanford Linear Accelerator Center (SLAC), showing the collision between a proton and a high-energy photon (electromagnetic radiation). The collision point is marked by the arrow; the track of the photon is not visible because only charged particles leave tracks in a bubble chamber. Several particle paths are seen branching from the collision site heading toward the bottom of the image. The tight spirals elsewhere in the photo are caused by electrons whose trajectories are strongly curved by the applied magnetic field.

Gas Ionization Counters

► The Geiger counter can detect only β and γ radiation. The α -particles cannot penetrate the walls or window of the tube.

A common gas ionization counter is the **Geiger–Müller counter** (Figure 22-5). Radiation enters the tube through a thin window. Windows of different stopping powers can be used to admit only radiation of certain penetrating powers.

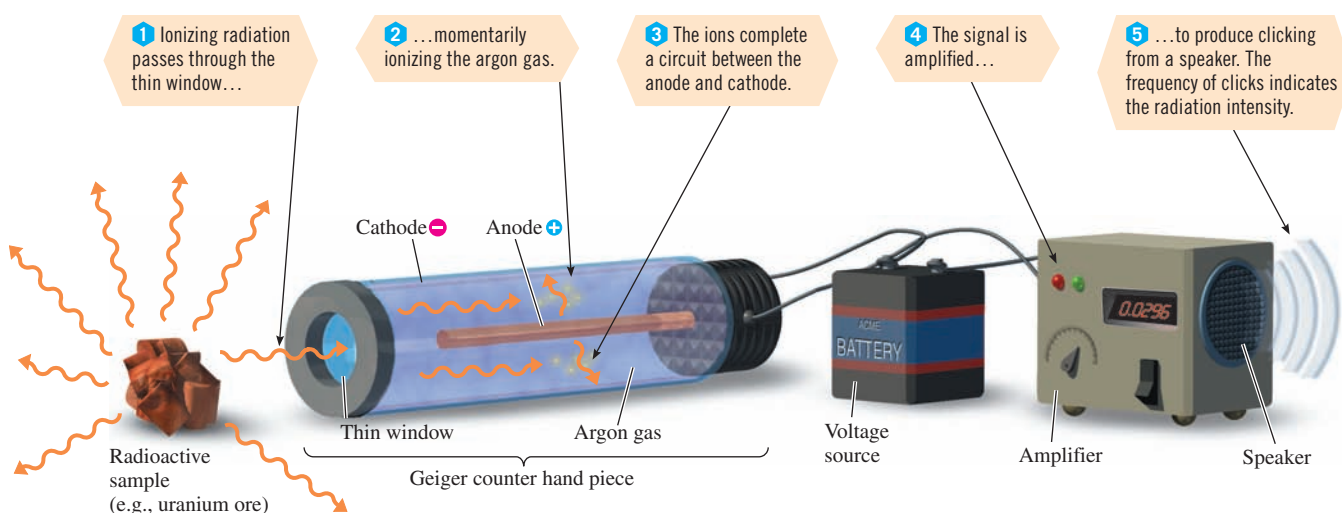


Figure 22-5 The principle of operation of a gas ionization counter. The center wire is positively charged, and the shell of the tube is negatively charged. When radiation enters through the window, it ionizes one or more gas atoms. The electrons are attracted to the central wire, and the positive ions are drawn to the shell. This constitutes a pulse of electric current, which is amplified and displayed on the meter or other readout.

22-10 Rates of Decay and Half-Life

Radionuclides have different stabilities and decay at different rates. Some decay nearly completely in a fraction of a second and others only after millions of years. The rates of all radioactive decays are independent of temperature and obey *first-order kinetics*. In Section 16-3, we saw that the rate of a first-order process is proportional to the concentration of only one substance. The rate law and the integrated rate equation for a first-order process (see Section 16-4) are

$$\text{rate of decay} = k[A] \quad \text{and} \quad \ln\left(\frac{A_0}{A}\right) = akt$$

Here A represents the amount of decaying radionuclide of interest remaining after some time t , and A_0 is the amount present at the beginning of the observation. The variable k is the rate constant, which is different for each radionuclide. Each atom decays independently of the others, so the stoichiometric coefficient a is *always* 1 for radioactive decay. We can therefore drop it from the calculations in this chapter and write the integrated rate equation as

$$\ln\left(\frac{A_0}{A}\right) = kt$$

Because A_0/A is a ratio, A_0 and A can represent either molar concentrations of a reactant or masses of a reactant. The rate of radioactive disintegrations follows first-order kinetics, so it is proportional to the amount of A present; we can write the integrated rate equation in terms of N , the number of disintegrations per unit time:

$$\ln\left(\frac{N_0}{N}\right) = kt$$

In nuclear chemistry, the decay rate is usually expressed in terms of the **half-life**, $t_{1/2}$, of the process. This is the amount of time required for half of the original sample to react. For a first-order process, $t_{1/2}$ is given by the equation

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

The isotope strontium-90 was introduced into the atmosphere by the atmospheric testing of nuclear weapons. Strontium is chemically similar to calcium, so strontium-90 now occurs with Ca in measurable quantities in milk, bones, and teeth as a result of its presence in food and water supplies. Strontium-90 is a radionuclide that undergoes beta emission with a half-life of 28.8 years. It may cause leukemia, bone cancer, and other related disorders. If we begin with a 16- μg sample of $^{90}_{38}\text{Sr}$, 8 μg will remain after one half-life of 28.8 years. After 57.6 years, 4 μg will remain; after 86.4 years, 2 μg ; and so on (Figure 22-6).

Because all radioactive decay follows first-order kinetics, a similar plot for any radionuclide shows the same shape of *exponential decay curve*. About ten half-lives (288 years for $^{90}_{38}\text{Sr}$) must pass for any radionuclide to lose 99.9% of its radioactivity.

► The reactant coefficient a is *always* 1 for radioactive decay.

► The amounts A_0 and A are usually given as masses (grams, milligrams, micrograms, etc.), but can be expressed in any convenient units.

► In 1963, a treaty was signed by the United States, the Soviet Union, and the United Kingdom prohibiting the further testing of nuclear weapons in the atmosphere. Since then, strontium-90 has been disappearing from the air, water, and soil according to the curve in Figure 22-6. So the treaty has largely accomplished its aim up to the present.

Unless otherwise noted, all content on this page is © Cengage Learning.

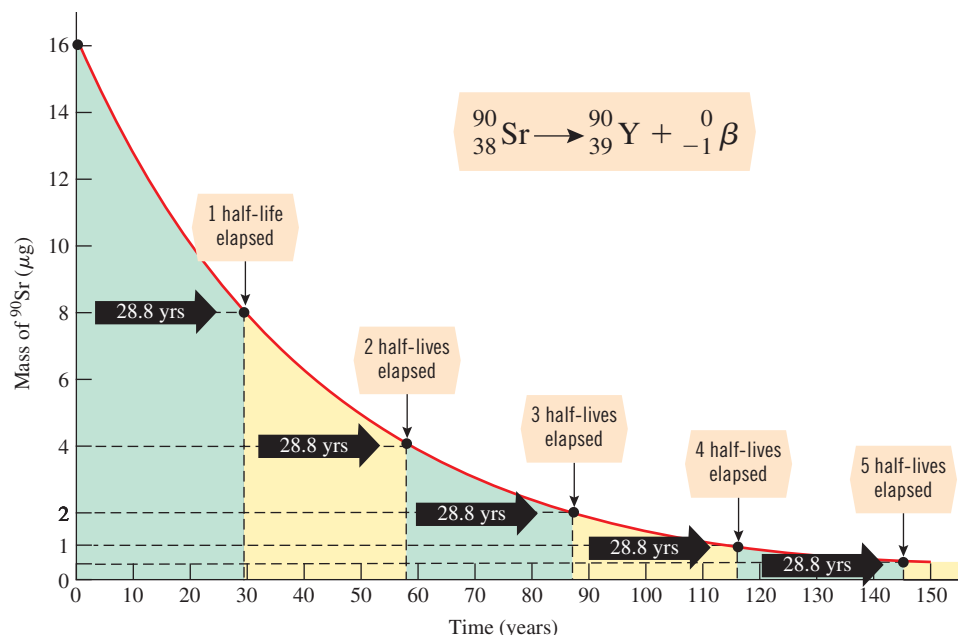
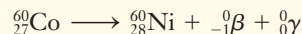


Figure 22-6 The decay of a 16- μg sample of $^{90}_{38}\text{Sr}$, a radioactive nuclide with a half-life of 28.8 years.

► Gamma rays destroy both cancerous and normal cells, so the beams of gamma rays must be directed as nearly as possible at only cancerous tissue.

EXAMPLE 22-4 Rate of Radioactive Decay

The “cobalt treatments” used in medicine to arrest certain types of cancer rely on the ability of gamma rays to destroy cancerous tissues. Cobalt-60 decays with the emission of beta particles and gamma rays, with a half-life of 5.27 years.



How much of a 3.42- μg sample of cobalt-60 remains after 30.0 years?

Plan

We determine the value of the specific rate constant, k , from the given half-life. This value is then used in the first-order integrated rate equation to calculate the amount of cobalt-60 remaining after the specified time.

Solution

We first determine the value of the specific rate constant.

$$t_{1/2} = \frac{0.693}{k} \quad \text{so} \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5.27 \text{ y}} = 0.131 \text{ y}^{-1}$$

This value can now be used to determine the ratio of A_0 to A after 30.0 years.

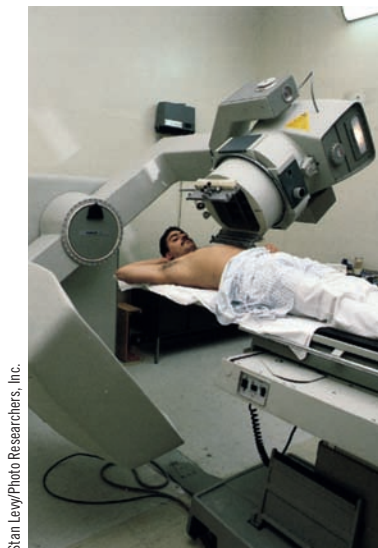
$$\ln\left(\frac{A_0}{A}\right) = kt = 0.131 \text{ y}^{-1}(30.0 \text{ y}) = 3.93$$

Taking the inverse $\ln$ of both sides, $\frac{A_0}{A} = 51$.

$$A_0 = 3.42 \mu\text{g}, \text{ so}$$

$$A = \frac{A_0}{51} = \frac{3.42 \mu\text{g}}{51} = 0.067 \mu\text{g } ^{60}_{27}\text{Co} \text{ remains after 30.0 years.}$$

You should now work Exercise 54.



Stan Levy/Photo Researchers, Inc.

The γ -radiation from ^{60}Co is used to treat cancers near the surface of the body.

Unless otherwise noted, all content on this page is © Cengage Learning.

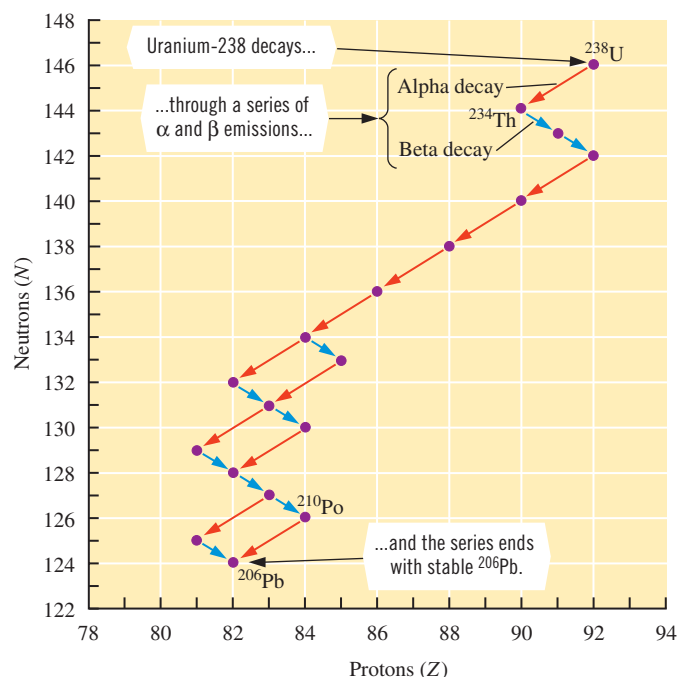
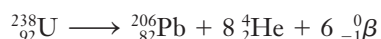


Figure 22-7 The ^{238}U decay series. Steps that occur by alpha emission are shown in red; beta emissions are shown in blue. See Table 22-4 for another representation of this and other decay series, including half-lives.

22-11 Decay Series

Many radionuclides cannot attain nuclear stability by only one nuclear reaction. Instead, they decay in a series of steps. For any particular decay step, the decaying nuclide is called the **parent** nuclide, and the product nuclide is the **daughter**.

Uranium-238 decays by alpha emission to thorium-234 in the first step of one series. Thorium-234 subsequently emits a beta particle to produce protactinium-234 in the second step. This series can be summarized as shown in Figure 22-7 and in Table 22-4a. The *net* reaction for the ^{238}U series is



“Branchings” are possible at various points in the chain. That is, two successive decays may be replaced by alternative decays, but they always result in the same final product. There are also decay series of varying lengths starting with some of the artificially produced radionuclides (see Section 22-13).

A few such series are known to occur in nature. Two begin with isotopes of uranium, ^{238}U and ^{235}U , and one begins with ^{232}Th . All three of these end with a stable isotope of lead ($Z = 82$). Table 22-4 outlines in detail the ^{238}U , ^{235}U , and ^{232}Th disintegration series, showing half-lives.

► Mass and charge balance for the decay series of $^{238}_{92}\text{U}$:

$$\begin{aligned} \text{mass: } 238 &\longrightarrow 206 + 8(4) + 6(0) = 238 \\ \text{charge: } 92 &\longrightarrow 82 + 8(+2) + 6(-1) = 92 \end{aligned}$$

22-12 Uses of Radionuclides

Radionuclides have practical uses because they decay at known rates. Some applications make use of the radiation that is continuously emitted by radionuclides.

Radioactive Dating

The ages of articles of organic origin can be estimated by *radiocarbon dating*. The radioisotope carbon-14 is produced continuously in the upper atmosphere as nitrogen atoms capture cosmic-ray neutrons.

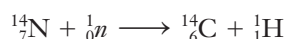
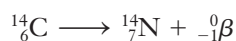


Table 22-4 Emissions and Half-Lives of the Natural Radioactive Decay Series*

(a) ^{238}U Series	(b) ^{235}U Series	(c) ^{232}Th Series
$^{238}_{92}\text{U} \rightarrow \alpha$ $4.51 \times 10^9 \text{ y}$ $^{234}_{90}\text{Th} \rightarrow \beta$ 24.1 d $^{234}_{91}\text{Pa} \rightarrow \beta$ 6.75 h $^{234}_{92}\text{U} \rightarrow \alpha$ $2.47 \times 10^5 \text{ y}$ $^{230}_{90}\text{Th} \rightarrow \alpha$ $8.0 \times 10^4 \text{ y}$ $^{226}_{88}\text{Ra} \rightarrow \alpha$ $1.60 \times 10^3 \text{ y}$ $^{222}_{86}\text{Rn} \rightarrow \alpha$ 3.82 d $\beta \leftarrow ^{218}_{84}\text{Po} \rightarrow \alpha$ 0.04% 3.05 m $\alpha \leftarrow ^{218}_{85}\text{At} \rightarrow \beta$ 2 s 26.8 m $\beta \leftarrow ^{214}_{83}\text{Bi} \rightarrow \alpha$ 99.96% 19.7 m $\alpha \leftarrow ^{214}_{84}\text{Po} \rightarrow \beta$ $1.6 \times 10^{24} \text{ s}$ 1.32 m 20.4 y $\beta \leftarrow ^{210}_{83}\text{Bi} \rightarrow \alpha$ 100% 5.01 d $\alpha \leftarrow ^{210}_{84}\text{Po} \rightarrow \beta$ 138 d 4.19 m $^{206}_{82}\text{Pb}$	$^{235}_{92}\text{U} \rightarrow \alpha$ $7.1 \times 10^8 \text{ y}$ $^{231}_{90}\text{Th} \rightarrow \beta$ 25.5 h $^{231}_{91}\text{Pa} \rightarrow \alpha$ $3.25 \times 10^4 \text{ y}$ $\beta \leftarrow ^{227}_{89}\text{Ac} \rightarrow \alpha$ 98.8% 21.6 y $\alpha \leftarrow ^{227}_{90}\text{Th} \rightarrow \beta$ 18.2 d 22 m $^{223}_{88}\text{Ra} \rightarrow \alpha$ 11.4 d $^{219}_{86}\text{Rn} \rightarrow \alpha$ 4.00 s $\beta \leftarrow ^{215}_{84}\text{Po} \rightarrow \alpha$ $5 \times 10^{-4}\%$ $1.78 \times 10^{-3} \text{ s}$ $\alpha \leftarrow ^{215}_{85}\text{At} \rightarrow \beta$ 10^{-4} s 36.1 m $\beta \leftarrow ^{211}_{83}\text{Bi} \rightarrow \alpha$ 99.7% 2.16 m $\alpha \leftarrow ^{211}_{84}\text{Po} \rightarrow \beta$ 0.52 s 4.79 m $^{207}_{82}\text{Pb}$	$^{232}_{90}\text{Th} \rightarrow \alpha$ $1.41 \times 10^{10} \text{ y}$ $^{228}_{88}\text{Ra} \rightarrow \beta$ 6.7 y $^{228}_{89}\text{Ac} \rightarrow \beta$ 6.13 h $^{228}_{90}\text{Th} \rightarrow \alpha$ 1.91 y $^{224}_{88}\text{Ra} \rightarrow \alpha$ 3.64 d $^{220}_{86}\text{Rn} \rightarrow \alpha$ 55.3 s $\beta \leftarrow ^{216}_{84}\text{Po} \rightarrow \alpha$ 0.014% 0.14 s $\alpha \leftarrow ^{216}_{85}\text{At} \rightarrow \beta$ $3 \times 10^{-4} \text{ s}$ 10.6 h $\beta \leftarrow ^{212}_{83}\text{Bi} \rightarrow \alpha$ 66.3% 60.6 m $\alpha \leftarrow ^{212}_{84}\text{Po} \rightarrow \beta$ $3.0 \times 10^{-7} \text{ s}$ 3.10 m $^{208}_{82}\text{Pb}$

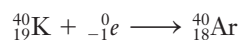
*Abbreviations are y, year; d, day; m, minute; and s, second. Less prevalent decay branches are shown in blue.

The carbon-14 atoms react with oxygen molecules to form $^{14}\text{CO}_2$. This process continually supplies the atmosphere with radioactive $^{14}\text{CO}_2$, which is removed from the atmosphere by photosynthesis. The intensity of cosmic rays is related to the sun's activity. As long as this remains constant, the amount of $^{14}\text{CO}_2$ in the atmosphere remains constant. $^{14}\text{CO}_2$ is incorporated into living organisms just as ordinary $^{12}\text{CO}_2$ is, so a certain fraction of all carbon atoms in living substances is carbon-14. This decays with a half-life of 5730 years.



After death, the plant no longer carries out photosynthesis, so it no longer takes up $^{14}\text{CO}_2$. Other organisms that consume plants for food stop doing so at death. As the ^{14}C in dead tissue then decays, its β -emissions decrease with the passage of time. The activity per gram of carbon is a measure of the length of time elapsed since death. Comparison of ages of ancient trees calculated from ^{14}C activity with those determined by counting rings indicates that cosmic ray intensity has varied somewhat throughout history. The calculated ages can be corrected for these variations. The carbon-14 technique is useful only for dating objects less than 50,000 years old. Older objects have too little activity to be dated accurately.

The *potassium–argon* and *uranium–lead* methods are used for dating older objects. Potassium-40 decays to argon-40 with a half-life of 1.3 billion years.



Because of its long half-life, potassium-40 can be used to date objects up to 1 billion years old by determination of the ratio of $^{40}_{19}\text{K}$ to $^{40}_{18}\text{Ar}$ in the sample. The uranium–lead method is based on the natural uranium-238 decay series, which ends with the production of stable lead-206. This method is used for dating uranium-containing minerals several billion years old because this series has an even longer half-life. All the ^{206}Pb in such minerals is assumed to have come from ^{238}U . Because of the very long half-life of $^{238}_{92}\text{U}$, 4.5 billion years, the amounts of intermediate nuclei can be neglected. A meteorite that was 4.6 billion years old fell in Mexico in 1969. Results of $^{238}\text{U}/^{206}\text{Pb}$ studies on such materials of extraterrestrial origin suggest that our solar system was formed several billion years ago.



© Reuters/Corbis

In 1992, hikers in the Italian Alps found the remains of a man who had been frozen in a glacier for about 4000 years. This discovery was especially important because of the unusual preservation of tissues, garments, and personal belongings. Radiocarbon dating is used to estimate the ages of archaeological finds such as these.

EXAMPLE 22-5 Radiocarbon Dating

A piece of wood taken from a cave dwelling in New Mexico is found to have a carbon-14 activity (per gram of carbon) only 0.636 times that of wood cut today. Estimate the age of the wood. The half-life of carbon-14 is 5730 years.

Plan

As we did in Example 22-4, we determine the specific rate constant k from the known half-life. The time required to reach the present fraction of the original activity is then calculated from the first-order decay equation.

Solution

First we find the first-order specific rate constant for ^{14}C .

$$t_{1/2} = \frac{0.693}{k} \quad \text{or} \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ y}} = 1.21 \times 10^{-4} \text{ y}^{-1}$$

The present ^{14}C activity, N (disintegrations per unit time), is 0.636 times the original activity, N_0 .

$$N = 0.636 N_0$$

We substitute into the first-order decay equation

$$\ln\left(\frac{N_0}{N}\right) = kt$$

$$\ln\left(\frac{N_0}{0.636 N_0}\right) = (1.21 \times 10^{-4} \text{ y}^{-1})t$$

We cancel N_0 and solve for t .

$$\ln\left(\frac{1}{0.636}\right) = (1.21 \times 10^{-4} \text{ y}^{-1})t$$

$$0.452 = (1.21 \times 10^{-4} \text{ y}^{-1})t \quad \text{or} \quad t = 3.74 \times 10^3 \text{ y (or 3740 y)}$$

You should now work Exercises 58 and 62.

► Since more than 50% of the activity remains, it is reasonable that the item is less than 5730 years old.

EXAMPLE 22-6 Uranium–Lead Dating

A sample of uranium ore is found to contain 4.64 mg of ^{238}U and 1.22 mg of ^{206}Pb . Estimate the age of the ore. The half-life of ^{238}U is 4.51×10^9 years.

Plan

The original mass of ^{238}U is equal to the mass of ^{238}U remaining plus the mass of ^{238}U that decayed to produce the present mass of ^{206}Pb . We obtain the specific rate constant, k , from the known half-life. Then we use the ratio of original ^{238}U to remaining ^{238}U to calculate the time elapsed, with the aid of the first-order integrated rate equation.

Solution

First we calculate the amount of ^{238}U that must have decayed to produce 1.22 mg of ^{206}Pb , using the isotopic masses.

$$\underline{\quad} \text{ mg } ^{238}\text{U} = 1.22 \text{ mg } ^{206}\text{Pb} \times \frac{238 \text{ mg } ^{238}\text{U}}{206 \text{ mg } ^{206}\text{Pb}} = 1.41 \text{ mg } ^{238}\text{U}$$

Thus, the sample originally contained $4.64 \text{ mg} + 1.41 \text{ mg} = 6.05 \text{ mg}$ of ^{238}U .

We next evaluate the specific rate (disintegration) constant, k .

$$t_{1/2} = \frac{0.693}{k} \quad \text{so} \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.51 \times 10^9 \text{ y}} = 1.54 \times 10^{-10} \text{ y}^{-1}$$

Now we calculate the age of the sample, t .

$$\ln\left(\frac{A_0}{A}\right) = kt$$

$$\ln\left(\frac{6.05 \text{ mg}}{4.64 \text{ mg}}\right) = (1.54 \times 10^{-10} \text{ y}^{-1})t$$

$$\ln 1.30 = (1.54 \times 10^{-10} \text{ y}^{-1})t$$

$$\frac{0.262}{1.54 \times 10^{-10} \text{ y}^{-1}} = t \quad \text{or} \quad t = 1.70 \times 10^9 \text{ years}$$

The ore is approximately 1.7 billion years old.

You should now work Exercise 76.

Medical Uses

The use of cobalt radiation treatments for cancerous tumors was described in Example 22-4. Several other nuclides are used in medicine as **radioactive tracers** (also called *radiopharmaceuticals*). Radioisotopes of an element have the same chemical properties as stable isotopes of the same element, so they can be used to “label” the presence of an element in compounds. A radiation detector can be used to follow the path of the element throughout the body. Modern computer-based techniques allow construction of an image of the area of the body where the radioisotope is concentrated. Salt solutions containing ^{24}Na can be injected into the bloodstream to follow the flow of blood and locate obstructions in the circulatory system. Thallium-201 tends to concentrate in healthy heart tissue, whereas technetium-99 concentrates in abnormal heart tissue. The two can be used together to survey damage from heart disease.

Iodine-123 concentrates in the thyroid gland, liver, and certain parts of the brain. This radioisotope is used to monitor goiter and other thyroid problems, as well as liver and brain tumors. One of the most useful radioisotopes in medical applications in recent years

► This isotope of iodine is also used in the treatment of thyroid cancer. Because of its preferential absorption in the thyroid gland, it delivers radiation where it is needed.

Unless otherwise noted, all content on this page is © Cengage Learning.

CHEMISTRY IN USE

Household Radon Exposure and Lung Cancer

Thanks to the Surgeon General's warnings on cigarette packages, most people are aware that smoking is the most common cause of lung cancer. But can you name the next most common? Few would guess that it's a noble gas, radon, and that this unhealthy element is almost certainly present in their home.

Radon has many unstable isotopes. The bad actor for humans is ^{222}Rn , a dense, odorless, colorless gas that is part of the ^{238}U decay chain (see Table 22-4). Radon is a major contributor to the background radiation dose experienced by the general population and the greatest natural source of radiation. (Other significant sources are cosmic radiation, particularly at high altitudes, and medical procedures.)

According to the World Health Organization, radon is responsible for between 3 and 14% of lung cancers. The Environmental Protection Agency (EPA) estimates that 21,000 cases of cancer in America each year are radon-related. The main damage to lung tissues is caused by the decay products ^{218}Po and ^{214}Po . When these species decay further, they emit alpha particles that harm DNA in the lung epithelium. Smokers are particularly at risk due to the elevated susceptibility of their lungs to cancer.

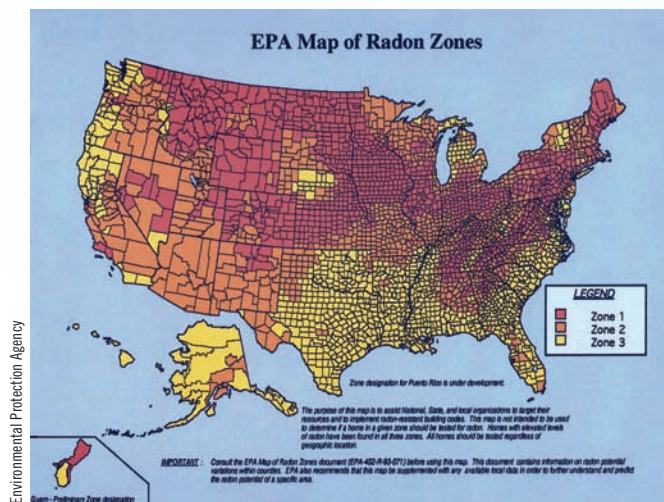
Radioactive decay is probably not high on your list of household worries, unless you happen to live next door to a missile silo or Three Mile Island. However, private homes are the locations of greatest radon health concern simply because people spend so much time in them. Uranium decay-chain elements occur naturally in geologic formations and thus ^{222}Rn is continually formed underground. It migrates upward through the

pores and cracks of rocks and soils, and then into cracks, joints, and gaps in any buildings directly above. This migration is driven by the pressure differential between surface air (comparatively low) and the rocks and groundsoil (comparatively high). The radon is eventually concentrated in the building interiors and inhaled by the people living or working there.

The average indoor residential radon level in the United States is about 1.3 picocuries per liter (pCi/L), over three times the average outdoor level of ~ 0.4 pCi/L. While there is no safe level of radon, the "action level" for mitigation set by the EPA is 4 pCi/L. (One curie of radioactivity is equivalent to the quantity of a given nuclide that provides 3.700×10^{10} disintegrations per second). Radon levels are often evaluated at the time of a house purchase. However, testing can be carried out at any time by a professional or with a self-test kit.

Active soil depressurization (ASD) is the most common technique used to mitigate high radon levels in homes, and typically lowers concentrations by 50 to 99%. ASD relies on a simple, controlled alteration of the air-soil pressure differential. A suction point (open-ended pipe) is installed underneath the slab or floor of the house in a small excavated area where radon can collect. This pipe is connected by additional pipe to a continuously operating exhaust fan with a rooftop outlet. The vacuum effect of the fan pulls the radon-containing air from the excavated area into the pipe and ejects it above the roof, bypassing the interior of the house (and the lungs of its inhabitants).

LISA SAUNDERS BAUGH



This EPA map shows predicted average indoor radon levels for all United States counties: Zone 1, >4 pCi/L; Zone 2, $2-4$ pCi/L; Zone 3, <2 pCi/L. Homes in the lower zones are not necessarily safer; houses with elevated radon levels have been found in all three zones.

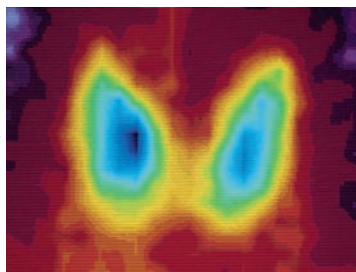


Photo taken by Lisa S. Baugh

The white pipe in these photos is part of an Active Soil Depressurization system to mitigate radon in a New Jersey home. The U-tube manometer liquid level differential in the photo indicates that the exhaust pump is functioning properly.

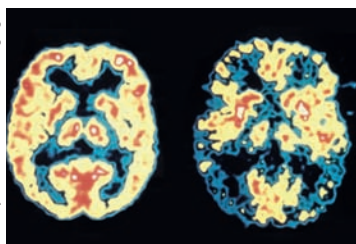
Unless otherwise noted, all content on this page is © Cengage Learning.

CNR/Photo Researchers, Inc.



A scan of the radiation released by radioactive iodine concentrated in thyroid tissue gives an image of the thyroid gland.

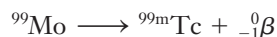
Courtesy of National Institution on Aging



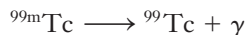
Positron emission tomography (PET) scans show differences in brain activity between a normal brain (*left*) and a brain affected by Alzheimer's disease (*right*). Glucose containing the radioactive isotope carbon-11 (^{11}C) was injected into the patients to obtain these images. When a carbon-11 isotope decays, it gives off a positron that immediately combines with an electron on another nearby atom. This matter–antimatter reaction converts these two particles into two high-energy gamma rays (180° apart) that are measured by a ring of detectors around the patient's head. Regions of the brain that are active consume more radioactive glucose and produce the brighter areas (red and yellow), while blue and black denote low or inactive portions.

► The procedure works because the female flies mate only once, so in an area highly populated with sterile males, the probability of a “productive” mating is very small.

is an isotope of technetium, an element that does not occur naturally on earth. This isotope, $^{99\text{m}}\text{Tc}$, is produced by the decay of ^{99}Mo .

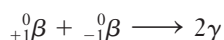


The “m” in the superscript $^{99\text{m}}\text{Tc}$ stands for “metastable.” This isotope is formed at a high energy, and then slowly decays by emitting gamma radiation.



This decay has a half-life of 6.0 hours—long enough for the preparation of the radiopharmaceutical and subsequent imaging of the patient, but short enough to avoid a harmful radiation dose to the patient. Technetium is a transition metal located in the center of the periodic table. It can exist in several oxidation states from -1 to $+7$. These can undergo a diversity of reactions that allow $^{99\text{m}}\text{Tc}$ to be incorporated into a variety of chemical forms. One chemical compound of $^{99\text{m}}\text{Tc}$ can be used to image the bones, another to image the liver, another to image the brain, and so on.

Another form of imaging that uses positron emitters (see Section 22-6) is *positron emission tomography (PET)*. Isotopes commonly used in this technique are short-lived positron emitters such as ^{11}C ($t_{1/2} = 20.4$ min), ^{13}N ($t_{1/2} = 9.98$ min), ^{15}O ($t_{1/2} = 2.05$ min), and ^{18}F ($t_{1/2} = 110$ min). The appropriate isotope is incorporated into a chemical that is normally taken up by the tissues that are being investigated, for instance carbon dioxide or glucose including ^{11}C or water including ^{15}O . This radioactive chemical can then be administered by inhalation or injection. The patient is then placed into a cylindrical gamma ray detector. When these radioisotopes decay, the emitted positron quickly encounters an electron and reacts in a matter–antimatter annihilation, to give off two gamma rays in opposite directions.



The directions of emission of millions of such pairs of gamma rays detected over several minutes allow for a computer reconstruction of an image of the tissue containing the positron emitter.

The energy produced by the decay of plutonium-238 can be converted into electrical energy and used in batteries for special long-life applications. Some heart pacemakers in the mid to late 1970s used ^{238}Pu as an energy source, but they now use safer lithium battery technology. Voyager 1 and 2 space probes, launched in 1977, used batteries based on $^{238}\text{PuO}_2$. These batteries are now near the end of their lifetimes after 35 years of constant operation.

Agricultural Uses

The pesticide DDT accumulates in fatty tissues, and is toxic to humans and animals repeatedly exposed to it. DDT persists in the environment for a long time. The DDT once used to control the screwworm fly was replaced by a radiological technique. Irradiating the male flies with gamma-rays alters their reproductive cells, sterilizing them. When great numbers of sterilized male flies are released in an infested area, they mate with females, that, of course, produce no offspring. This results in the reduction and eventual disappearance of the population.

Labeled fertilizers can also be used to study nutrient uptake by plants and to study the growth of crops. Gamma-irradiation of some foods allows them to be stored for longer periods without spoiling. For example, it retards the sprouting of potatoes and onions. In 1999, the FDA approved gamma-irradiation of red meat as a way to curb food-borne illnesses. In addition to reducing levels of *Listeria*, *Salmonella*, and other bacteria significantly, such irradiation is currently the only known way to completely eliminate the dangerous strain of *Escherichia coli* bacteria in red meat. Absorption of gamma-rays by matter produces no radioactive nuclides, so foods preserved in this way are *not* radioactive.



Courtesy of International Atomic Energy Agency

Moderate irradiation with gamma-rays from radioactive isotopes has kept the strawberries at the right fresh for 15 days, while those at the left are moldy. Such irradiation kills mold spores but does no damage to the food. The food does *not* become radioactive.

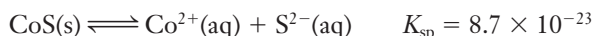
Industrial Uses

There are many applications of radiochemistry in industry and engineering. When great precision is required in the manufacture of strips or sheets of metal of definite thicknesses, the penetrating powers of various kinds of radioactive emissions are utilized. The thickness of the metal is correlated with the intensity of radiation passing through it. The flow of a liquid or gas through a pipeline can be monitored by injecting a sample containing a radioactive substance. Leaks in pipelines can also be detected in this way.

In addition to the ^{238}Pu -based heart pacemaker already mentioned, lightweight, portable power packs that use radioactive isotopes as fuel have been developed for other uses. Polonium-210, californium-242, and californium-244 have been used in such generators to power instruments for space vehicles and in polar regions. These generators can operate for years with only a small loss of power.

Research Applications

The pathways of chemical reactions can be investigated using radioactive tracers. When radioactive $^{35}\text{S}^{2-}$ ions are added to a saturated solution of cobalt sulfide in equilibrium with solid cobalt sulfide, the solid CoS becomes radioactive. This shows that sulfide ion exchange occurs between solid and solution in the solubility equilibrium.



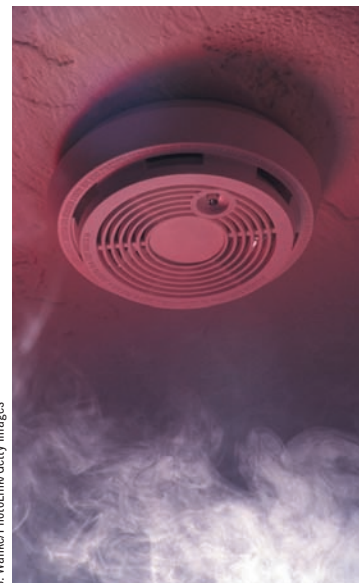
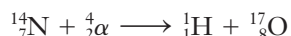
Photosynthesis is the process by which the carbon atoms in CO_2 are incorporated into glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, in green plants.



The process is far more complex than the net equation implies; it actually occurs in many steps and produces a number of intermediate products. By using labeled $^{14}\text{CO}_2$, which contains radioactive ^{14}C atoms, we can identify the intermediate molecules.

22-13 Artificial Transmutations of Elements

The first artificially induced nuclear reaction was carried out by Rutherford in 1915. He bombarded nitrogen-14 with alpha particles to produce an isotope of oxygen and a proton.



S. Wanke/PhotoLink/Getty Images

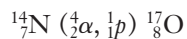
A weakly radioactive source such as americium is used in some smoke detectors. Radiation from the source ionizes the air to produce a weak current. Smoke particles interrupt the current flow by attracting the ions. This decrease in current triggers the alarm.



NASA/JPL-Caltech

The Curiosity Mars rover is powered by a $^{238}\text{PuO}_2$ thermoelectric battery. The rover requires more power than solar cells could provide.

Such reactions are often indicated in abbreviated form, with the bombarding particle and emitted subsidiary particles shown parenthetically between the parent and daughter nuclides.



Several thousand different artificially induced reactions have been carried out with bombarding particles such as neutrons, protons, deuterons (${}^2_1\text{H}$), alpha particles, and other small nuclei.

Bombardment with Positive Ions

A problem arises with the use of positively charged nuclei as projectiles. For a nuclear reaction to occur, the bombarding nuclei must actually collide with the target nuclei, which are also positively charged. Collisions cannot occur unless the projectiles have sufficient kinetic energy to overcome coulombic repulsion. The required kinetic energies increase with increasing atomic numbers of the target and of the bombarding particle.

Particle accelerators called **cyclotrons** (atom smashers) and **linear accelerators** have overcome the problem of repulsion. A cyclotron (Figure 22-8) consists of two hollow, D-shaped electrodes called “dees.” Both dees are in an evacuated enclosure between the poles of an electromagnet. The particles to be accelerated are introduced at the center in the gap between the dees. The dees are connected to a source of high-frequency alternating current that keeps them oppositely charged. The positively charged particles are attracted toward the negative dee. The magnetic field causes the path of the charged particles to curve 180° to return to the space between the dees. Then the charges are reversed on the dees, so the particles are repelled by the first dee (now positive) and attracted to the second. This repeated process is synchronized with the motion of the particles. They accelerate along a spiral path and eventually emerge through an exit hole oriented so that the beam hits the target atoms (Figure 22-9).

In a linear accelerator, the particles are accelerated through a series of tubes within an evacuated chamber (Figure 22-10). The odd-numbered tubes are at first negatively charged and the even ones positively charged. A positively charged particle is attracted toward the first tube. As it passes through that tube, the charges on the tubes are reversed so that the

► The first cyclotron was constructed by E. O. Lawrence (1901–1958) and M. S. Livingston at the University of California in 1930.

► The path of the particle is initially circular because of the interaction of the particle's charge with the electromagnet's field. As the particle gains energy, the radius of the path increases and the particle spirals outward.

► The first linear accelerator was built in 1928 by the German physicist Rolf Wideroe.

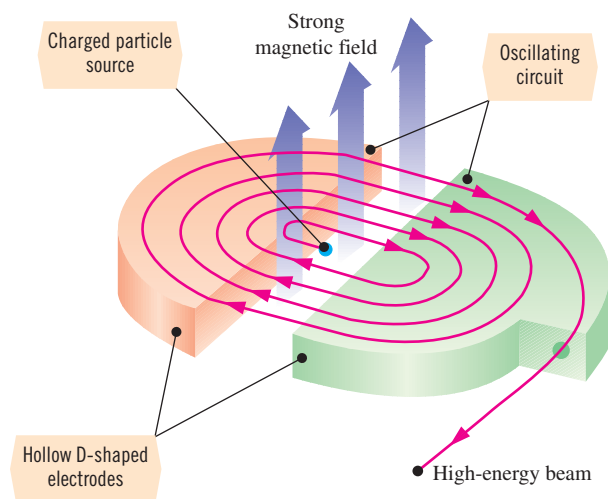


Figure 22-8 Schematic representation of a cyclotron.

Unless otherwise noted, all content on this page is © Cengage Learning.



Figure 22-9 The SLAC National Laboratory houses what used to be called the Stanford Linear Accelerator Center and is still commonly called that. The accelerator is 2 miles long and is the longest in the world.

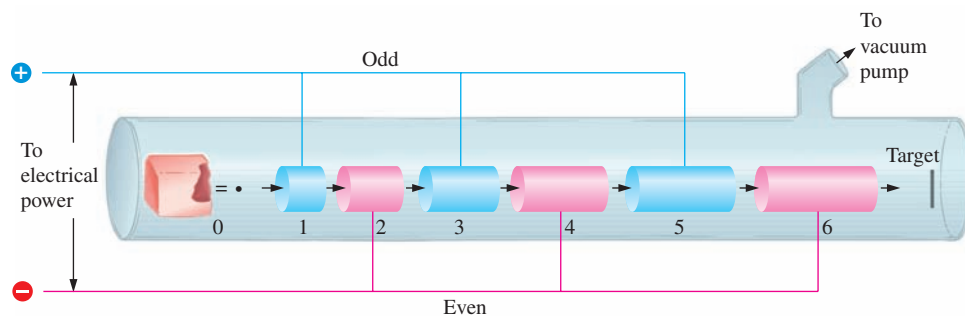
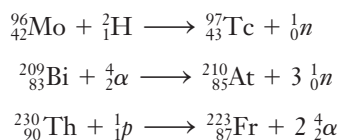


Figure 22-10 Diagram of an early type of linear accelerator. An alpha emitter is placed in the container at the left. Only those α -particles that happen to be emitted in line with the series of accelerating tubes can escape.

particle is repelled out of the first tube (now positive) and toward the second (negative) tube. Each time the particle nears the end of the second tube, the charges are again reversed. As this process is repeated, the particle is accelerated to very high velocities. The polarity is changed at constant frequency, so subsequent tubes are longer to accommodate the increased distance traveled by the accelerating particle per unit time. The bombardment target is located outside the last tube. If the initial polarities are reversed, negatively charged particles can also be accelerated. The longest linear accelerator, completed in 1966 at Stanford University, is about 2 miles long. It is capable of accelerating electrons to energies of nearly 20 GeV (see Figure 22-9).

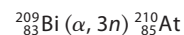
Many nuclear reactions have been induced by such bombardment techniques. At the time of development of particle accelerators, there were a few gaps among the first 92 elements in the periodic table. Particle accelerators were used between 1937 and 1941 to synthesize three of the four “missing” elements: numbers 43 (technetium), 85 (astatine), and 87 (francium).



Many hitherto unknown, unstable, artificial isotopes of known elements have also been synthesized so that their nuclear structures and behavior could be studied.

► One gigaelectron volt (GeV) = $1 \times 10^9 \text{ eV} = 1.60 \times 10^{-10} \text{ J}$. This is sometimes called 1 billion electron volts (BeV) in the United States.

► Mass and charge balance for alpha capture reaction



mass: $209 + 4 \longrightarrow 210 + 3(1)$
charge: $83 + 2 \longrightarrow 85 + 3(0)$

Neutron Bombardment

Neutrons bear no charge, so they are not repelled by nuclei as positively charged projectiles are. They do not need to be accelerated to produce bombardment reactions. Neutron



The CERN Large Hadron Collider, which spans the border between Switzerland and France, is more than 16 miles in circumference. The LHC recently provided evidence for the long-sought Higgs Boson subatomic particle.

Unless otherwise noted, all content on this page is © Cengage Learning.

beams can be generated in several ways. A frequently used method involves bombardment of beryllium-9 with alpha particles.



► Fast neutrons move so rapidly that they are likely to pass right through a target nucleus without reacting. Hence, the probability of a reaction is low, even though the neutrons may be very energetic.

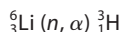
Nuclear reactors (Section 22-15) are also used as neutron sources. Neutrons ejected in nuclear reactions usually possess high kinetic energies and are called **fast neutrons**. When they are used as projectiles they cause reactions, such as (n, p) or (n, α) reactions, in which subsidiary particles are ejected. The fourth “missing” element, number 61 (promethium), was synthesized by fast neutron bombardment of neodymium-142.



Slow neutrons (“thermal” neutrons) are produced when fast neutrons collide with **moderators** such as hydrogen, deuterium, oxygen, or the carbon atoms in paraffin. These neutrons are more likely to be captured by target nuclei. Bombardments with slow neutrons can cause neutron-capture (n, γ) reactions.



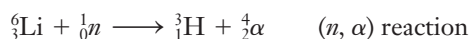
► Mass and charge balance for neutron capture reaction



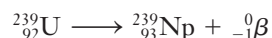
$$\text{mass: } 6 + 1 \longrightarrow 3 + 4$$

$$\text{charge: } 3 + 0 \longrightarrow 1 + 2$$

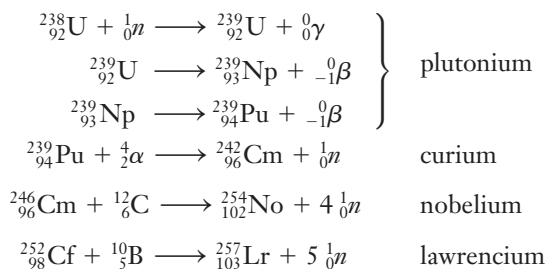
Slow neutron bombardment also produces the ${}^3\text{H}$ isotope (tritium).



E. M. McMillan (1907–1991) discovered the first transuranium element, neptunium, in 1940 by bombarding uranium-238 with slow neutrons.

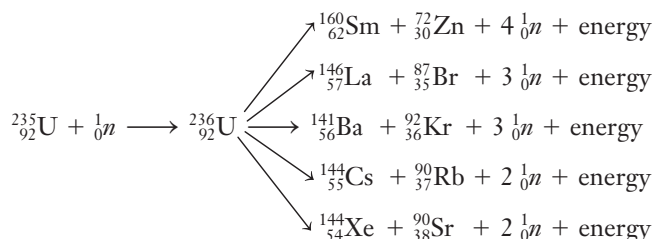


Several additional elements have been prepared by neutron bombardment or by bombardment of the nuclei so produced with positively charged particles. Some examples are



22-14 Nuclear Fission

Isotopes of some elements with atomic numbers above 80 are capable of undergoing fission in which they split into nuclei of intermediate masses and emit one or more neutrons. Some fissions are spontaneous; others require that the activation energy be supplied by bombardment. A given nucleus can split in many different ways, liberating enormous amounts of energy. Some of the possible fissions that can result from bombardment of fissionable uranium-235 with fast neutrons follow. The uranium-236 is a short-lived intermediate.



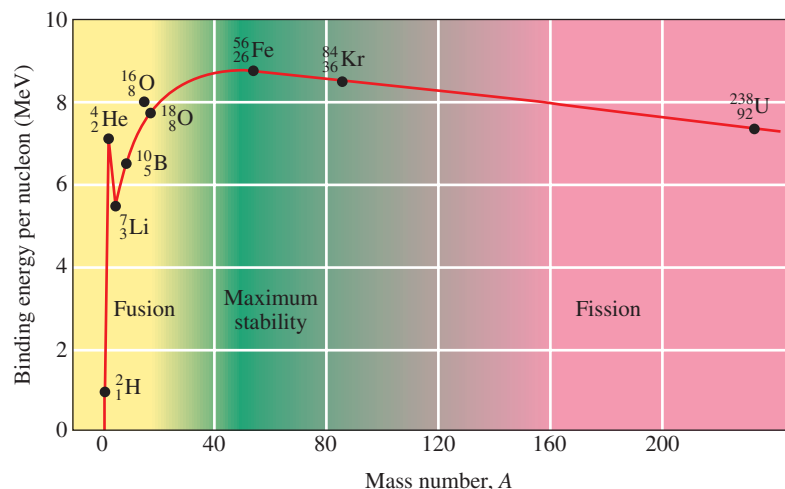


Figure 22-11 Variation in nuclear binding energy per nucleon with atomic mass. This plot shows the relative stability of the most stable isotopes of selected elements. The most stable nucleus is $^{56}_{26}\text{Fe}$, with a binding energy of 8.80 MeV per nucleon

$$1 \text{ MeV} = 1.60 \times 10^{-13} \text{ J}$$

Recall that the binding energy is the amount of energy that must be supplied to the nucleus to break it apart into subatomic particles. Figure 22-11 is a plot of binding energy per nucleon versus mass number. It shows that atoms of intermediate mass number have the highest binding energies per nucleon; therefore, they are the most stable. Thus, fission is an energetically favorable process for heavy atoms because atoms with intermediate masses and greater binding energies per nucleon are formed.

Which isotopes of which elements undergo fission? Experiments with particle accelerators have shown that every element with an atomic number of 80 or more has one or more isotopes capable of undergoing fission, provided they are bombarded at the right energy. Nuclei with atomic numbers between 89 and 98 fission spontaneously with long half-lives of 10^4 to 10^{17} years. Nuclei with atomic numbers of 98 or more fission spontaneously with shorter half-lives of a few milliseconds to 60.5 days. One of the *natural* decay modes of the transuranium elements is via spontaneous fission. In fact, all known nuclides with *mass numbers* greater than 250 do this because they are too big to be stable. Most nuclides with mass numbers between 225 and 250 do not undergo fission spontaneously (except for a few with extremely long half-lives). They can be induced to undergo fission when bombarded with particles of relatively low kinetic energies. Particles that can supply the required activation energy include neutrons, protons, alpha particles, and fast electrons. For nuclei lighter than mass 225, the activation energy required to induce fission rises very rapidly.

In Section 22-2, we discussed the stability of nuclei with even numbers of protons and even numbers of neutrons. We should not be surprised to learn that both ^{233}U and ^{235}U can be excited to fissionable states by slow neutrons much more easily than ^{238}U because they are less stable. It is so difficult to cause fission in ^{238}U that this isotope is said to be “nonfissionable.”

Typically, two or three neutrons are produced per fission reaction. These neutrons can collide with other fissionable atoms to repeat the process. If sufficient fissionable material, the **critical mass**, is contained in a small enough volume, a sustained **chain reaction** can result. If too few fissionable atoms are present, most of the neutrons escape and no chain reaction occurs. Figure 22-12 depicts a fission chain reaction.

In an atomic bomb, two subcritical portions of fissionable material are brought together to form a critical mass. A nuclear fission explosion results. A tremendous amount of heat energy is released, as well as many radionuclides whose effects are devastating to life and the environment. The radioactive dust and debris are called *fallout*.

► The term *nucleon* refers to a nuclear particle, either a neutron or a proton.

► The word “fission” can be used either as a noun (meaning the process) or as a verb (meaning to undergo the process).

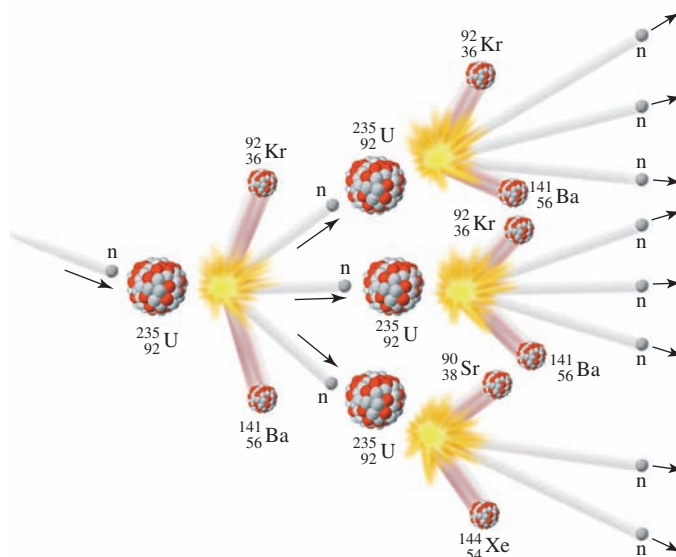


Figure 22-12 A self-propagating nuclear chain reaction. A stray neutron induces a single fission, liberating more neutrons. Each of them induces another fission, each of which is accompanied by release of two or three neutrons. The chain continues to branch in this way, very quickly resulting in an explosive rate of fission.

22-15 Nuclear Fission Reactors

In a nuclear fission reactor, the fission reaction is controlled by inserting materials to absorb some of the neutrons so that the mixture does not explode. The energy that is produced can be safely used as a heat source in a power plant.

Light Water Reactors

Most commercial nuclear power plants in the United States are “light water” reactors, moderated and cooled by ordinary water. Figure 22-13 is a schematic diagram of a light

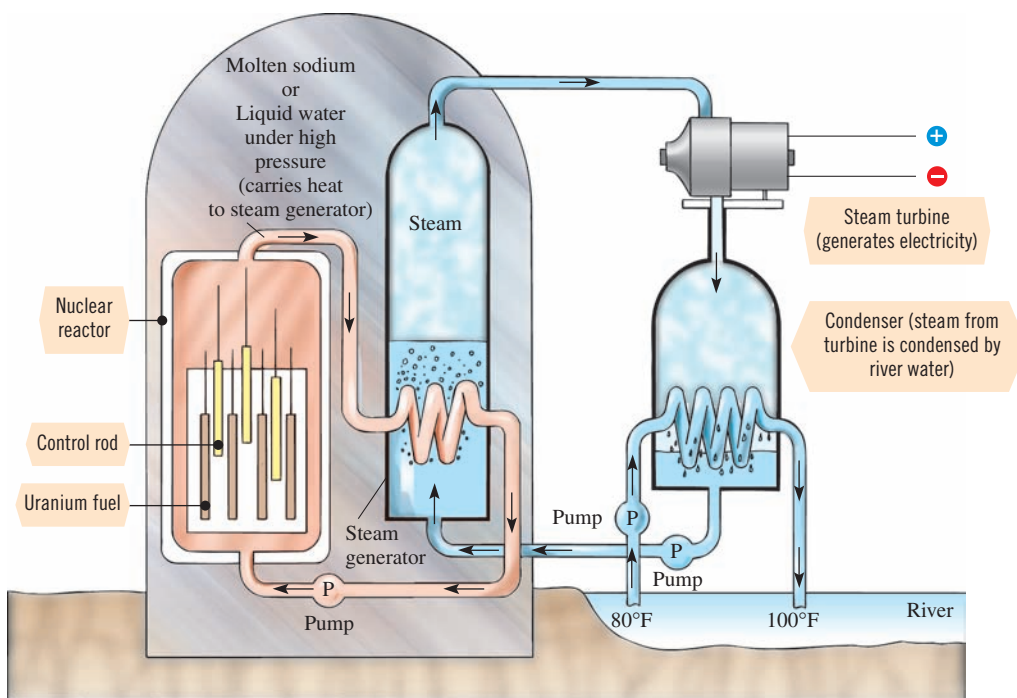


Figure 22-13 A schematic diagram of a light water reactor plant. This design includes two closed loops of water. The water that carries heat from the reactor to the steam generator is in a closed loop and is not released to the environment.

Unless otherwise noted, all content on this page is © Cengage Learning.

water reactor plant. The reactor core at the left replaces the furnace in which coal, oil, or natural gas is burned in a fossil fuel plant. Such a fission reactor consists of five main components: (1) fuel, (2) moderator, (3) control rods, (4) cooling system, and (5) shielding.

Fuel

Rods of U_3O_8 enriched in uranium-235 serve as the fuel. Unfortunately, uranium ores contain only about 0.7% $^{235}_{92}\text{U}$. Most of the rest is nonfissionable $^{238}_{92}\text{U}$. The enrichment is done in processing and reprocessing plants by separating gaseous $^{235}\text{UF}_6$ from $^{238}\text{UF}_6$, prepared from the ore. Separation by diffusion is based on the slower rates of diffusion of heavier gas molecules (see Section 12-14). Another separation procedure uses the ultracentrifuge.

A potentially more efficient method of enrichment would involve the use of sophisticated tunable lasers to ionize $^{235}_{92}\text{U}$ selectively and not $^{238}_{92}\text{U}$. The ionized $^{235}_{92}\text{U}$ could then be made to react with negative ions to form another compound, easily separated from the mixture. For this method to work, we must construct lasers capable of producing radiation monochromatic enough to excite one isotope and not the other—a difficult challenge.

Moderator

The fast neutrons ejected during fission are too energetic to be absorbed efficiently by other nuclei. Thus, they must be slowed by collisions with atoms of comparable mass that do not absorb them, called *moderators*. The most commonly used moderator is ordinary water, although graphite is sometimes used. The most efficient moderator is helium, which slows neutrons but does not absorb them all. The next most efficient is **heavy water** (deuterium oxide, $^2_1\text{H}_2\text{O}$ or $^2_1\text{D}_2\text{O}$). This is so expensive that it has been used chiefly in research reactors. A Canadian-designed power reactor that uses heavy water is more neutron-efficient than light water reactors. This design is the basis of the many reactors in Canada.

Control Rods

Cadmium and boron are good neutron absorbers.



The rate of a fission reaction is controlled by the use of movable control rods, usually made of cadmium or boron steel. They are automatically inserted in or removed from spaces between the fuel rods. The more neutrons absorbed by the control rods, the fewer fissions occur and the less heat is produced. Hence, the heat output is governed by the control system that operates the rods.

Cooling System

Two cooling systems are needed. First, the moderator itself serves as a coolant for the reactor. It transfers fission-generated heat to a steam generator. This converts water to steam. The steam then goes to turbines that drive generators to produce electricity. Another coolant (river water, seawater, or recirculated water) condenses the steam from the turbine, and the condensate is then recycled into the steam generator.

The danger of meltdown arises if a reactor is shut down quickly. The disintegration of radioactive fission products still goes on at a furious rate, fast enough to overheat the fuel elements and to melt them. So it is not enough to shut down the fission reaction. Efficient cooling must be continued until the short-lived isotopes are gone and the heat from their disintegration is dissipated. Only then can the circulation of cooling water be stopped.

The 1979 accident at Three Mile Island, near Harrisburg, Pennsylvania, was due to stopping the water pumps too soon *and* the inoperability of the emergency pumps. A combination of mechanical malfunctions, errors, and carelessness produced the overheating that damaged the fuel assembly. It did not and *could not explode*, although melting of the core material did occur. The 1986 accident at Chernobyl, in the USSR, involved a reactor



Uranium is deposited on the negative electrode in the electrorefining phase of fuel reprocessing. The crystalline mass is about 97% LiCl and KCl . The remaining 3% uranium chloride is responsible for the amethyst color.



Nuclear powered submarines, like the USS Maryland shown here, typically use pressurized water reactors and highly enriched nuclear fuel to provide more power from a smaller reactor. One stealth issue with nuclear subs is the need to cool the reactor, which leaves a trail of warm water that rises to the surface.

Unless otherwise noted, all content on this page is © Cengage Learning.

► The neutrons are the worst problem of radiation. The human body contains a high percentage of H_2O , which absorbs neutrons very efficiently. The neutron bomb produces massive amounts of neutrons and so is effective against people, but it does not produce the long-lasting radiation or blast damage of the fission atomic bomb.

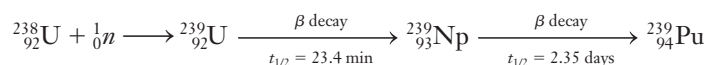
of a very different design and was far more serious. The effects of that disaster will continue for decades.

Shielding

It is essential that people and the surrounding countryside be adequately shielded from possible exposure to radioactive nuclides. The entire reactor is enclosed in a steel containment vessel. This is housed in a thick-walled concrete building. The operating personnel are further protected by a so-called biological shield, a thick layer of organic material made of compressed wood fibers. This absorbs the neutrons and beta and gamma rays that would otherwise be absorbed in the human body.

Breeder Reactors

The possibility of shortages in the known supply of $^{235}_{92}\text{U}$ has led to the development of **breeder reactors**, which can manufacture more fuel than they use. A breeder reactor is designed not only to generate electrical power but also to maximize neutron capture in the core by $^{238}_{92}\text{U}$. The fuel of a typical breeder reactor consists of the abundant but nonfissionable isotope $^{238}_{92}\text{U}$ mixed with $^{235}_{92}\text{U}$ or $^{239}_{94}\text{Pu}$, which produce neutrons when they undergo fission. Some of these neutrons are absorbed by $^{238}_{92}\text{U}$ to form $^{239}_{92}\text{U}$. This unstable uranium isotope soon leads, after two steps of beta emission, to $^{239}_{94}\text{Pu}$.



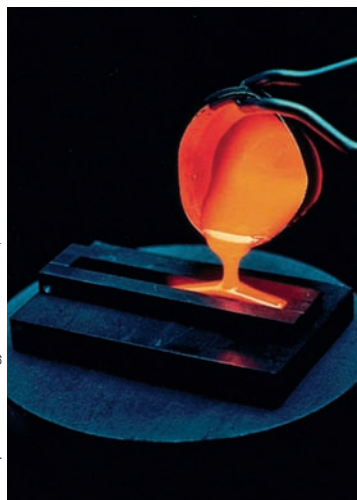
This fissionable $^{239}_{94}\text{Pu}$ can then be used as fuel in a reactor.

For every $^{235}_{92}\text{U}$ or $^{239}_{94}\text{Pu}$ nucleus that undergoes fission, more than one neutron is captured by $^{238}_{92}\text{U}$ to produce $^{239}_{94}\text{Pu}$. Thus, the breeder reactor can produce more fissionable material than it consumes. After about 7 years, enough $^{239}_{94}\text{Pu}$ can be collected to fuel a new reactor *and* to refuel the original one.

Nuclear Power: Hazards and Benefits

Controlled fission reactions in nuclear reactors are of great use and have even greater potential. The fuel elements of a nuclear reactor have neither the composition nor the extremely compact arrangement of the critical mass of a bomb. Thus, no possibility of nuclear explosion exists. However, various dangers are associated with nuclear energy generation. The possibility of “meltdown” has been discussed with respect to cooling systems in light water reactors. Proper shielding precautions must be taken to ensure that the radionuclides produced are always contained within vessels from which neither they nor their radiations can escape. Long-lived radionuclides from spent fuel must be stored underground in heavy, shock-resistant containers until they have decayed to the point that they are no longer biologically harmful. As examples, strontium-90 ($t_{1/2} = 28$ years) and plutonium-239 ($t_{1/2} = 24,000$ years) must be stored for 280 years and 240,000 years, respectively, before they lose 99.9% of their activities. Critics of nuclear energy contend that the containers could corrode over such long periods, or burst as a result of earth tremors, and that transportation and reprocessing accidents could cause environmental contamination with radionuclides. They claim that river water used for cooling is returned to the rivers with too much heat (thermal pollution), thus disrupting marine life. (It should be noted, though, that fossil fuel electric power plants cause the same thermal pollution for the same amount of electricity generated.) The potential for theft also exists. Plutonium-239, a fissionable material, could be stolen from reprocessing plants and used to construct atomic weapons.

Proponents of the development of nuclear energy argue that the advantages far outweigh the risks. Nuclear energy plants do not pollute the air with oxides of sulfur, nitrogen, carbon, and particulate matter, as fossil fuel electric power plants do. The big advantage of nuclear fuels is the enormous amount of energy liberated per unit mass of fuel. At present, nuclear reactors provide about 20% of the electrical energy consumed in the United States.



U.S. Department of Energy/Photo Researchers, Inc.

Nuclear waste may take centuries to decompose, so we cannot afford to take risks in its disposal. Suggested approaches include casting it into ceramics, as shown here, to eliminate the possibility of the waste dissolving in groundwater. The encapsulated waste could then be deposited in underground salt domes. Located in geologically stable areas, such salt domes have held petroleum and compressed natural gas trapped for millions of years. The political problems of nuclear waste disposal are at least as challenging as the technological ones. Refer to the Chemistry in Use box entitled “Managing Nuclear Wastes” in this chapter.

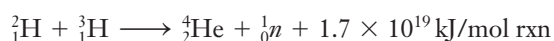
Unless otherwise noted, all content on this page is © Cengage Learning.

In some parts of Europe, where natural resources of fossil fuels are scarcer, the utilization of nuclear energy is higher. For instance, in France and Belgium, more than 80% of electrical energy is produced from nuclear reactors. With rapidly declining fossil fuel reserves, it appears likely that nuclear energy and solar energy will become increasingly important. Intensifying public concerns about nuclear power, however, may mean that further growth in energy production using nuclear power in the United States must await technological developments to overcome the remaining hazards.

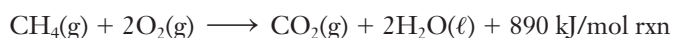
22-16 Nuclear Fusion

Fusion, the joining of light nuclei to form heavier nuclei, is favorable for the very light atoms. In both fission and fusion, the energy liberated is equivalent to the loss of mass that accompanies the reactions. Much greater amounts of energy per unit mass of *reacting atoms* are produced in fusion than in fission.

Spectroscopic evidence indicates that the sun is a tremendous fusion reactor consisting of 73% H, 26% He, and 1% other elements. Its major fusion reaction is thought to involve the combination of a deuteron, ${}^2_1\text{H}$, and a triton, ${}^3_1\text{H}$, at tremendously high temperatures to form a helium nucleus and a neutron with the release of a huge amount of energy.



Thus, solar energy is actually a form of fusion energy. A fusion reaction releases a tremendous amount of energy. Compare the energy of the deuteron/triton fusion reaction with that released by the burning of the methane in natural gas (see Section 15-1).



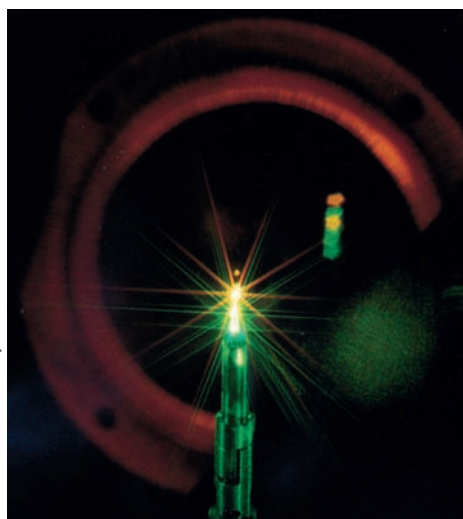
Fusion reactions are accompanied by even greater energy production per unit mass of reacting atoms than are fission reactions. They can be initiated only by extremely high temperatures, however. This is why fusion reactions are often referred to as **thermonuclear** reactions. The fusion of ${}^2_1\text{H}$ and ${}^3_1\text{H}$ occurs at the lowest temperature of any fusion reaction known, but even this is 40,000,000 K! Such temperatures exist in the sun and

Photo courtesy of National Nuclear Security Administration/Nevada Site Office



The explosion of a thermonuclear (hydrogen) bomb releases tremendous amounts of energy. If we could learn how to control this process, we would have nearly limitless amounts of energy.

Lawrence Livermore Laboratory



Nuclear fusion provides the energy of our sun and other stars. Development of controlled fusion as a practical source of energy requires methods to initiate and contain the fusion process. Here a very powerful laser beam has initiated a fusion reaction in a 1-mm target capsule that contained deuterium and tritium. In a 0.5-picosecond burst, 10^{13} neutrons were produced by the reaction ${}^2_1\text{H} + {}^3_1\text{H} \longrightarrow {}^4_2\text{He} + {}^1_0n$.

Unless otherwise noted, all content on this page is © Cengage Learning.

Managing Nuclear Wastes

Some may consider a career in managing nuclear waste as being just about the worst job anyone would ever want, but hundreds of technically trained people have spent years working to solve the problems associated with nuclear power. The major part of the continuing challenge is political. Nuclear power plants generate about 20% of the electricity in the United States. Most of the high-level nuclear waste (HLW) that is generated from nuclear power plants—in the form of spent nuclear fuel (SNF)—is generated where many people live, in the eastern half of the United States. The safest place for a repository is away from people, in a dry, remote location, probably in the western United States, where there are fewer people (and fewer votes!).

SNF constitutes about half of the HLW in the United States. The other half comes from the construction and existence of nuclear weapons. All HLW is a federal responsibility. About 90% of the radioactivity in nuclear waste is from HLW. The largest volume of nuclear waste is low-level waste (LLW), and that is mostly the responsibility of the state (or group of states) in which it is generated. LLW is rather awkwardly defined, being everything that is neither HLW nor defense waste and consists of wastes from hospitals; pharmaceutical labs; research labs; and the moon suits, tools, and the like from nuclear power plants. In the eastern United States, most of the LLW is in the form of the plastic beads that make up the ion-exchange resins used in nuclear power plants to clean various loops of water used in power production.

Plutonium wastes from the Los Alamos National Laboratory in northern New Mexico were trucked for the first time to the federal Waste Isolation Pilot Plant in Carlsbad in March 1999. The 600 pounds (270 kg) of waste consisted of plutonium-contaminated clothing and metal cans, packed in boxes and stainless steel containers. Most of the material was from the laboratory's manufacture of nuclear batteries used in NASA's deep space probes and will be buried in the depository carved out of ancient salt caverns about half a mile (0.8 km) below ground.

Most current attention is focused on SNF for two reasons. It is highly radioactive, and it can be seen as a "local" problem because it is made where electric customers live. Europe has reprocessing plants to recover the unused fissionable material for new fuel, but the United States disallowed the practice in the 1970s. This partially explains why spent fuel rods have been piling up at US nuclear plants.

Research focused on Yucca Mountain, Nevada, at the western edge of the National Test Site, for its suitability as a nuclear waste repository for SNF and some defense waste. In July 2002, after both houses of the US Congress voted to override a veto by the State of Nevada, President George W. Bush signed the bill making Yucca Mountain the central repository for the nation's nuclear waste. Many political leaders and residents of Nevada strongly opposed this plan, and they seriously question

that nuclear waste can be safely kept out of the human environment for 10,000 years, as is required under the federal Nuclear Waste Policy Act. Funding for the Yucca Mountain project was terminated in 2011 by Congress, but the controversy on where to store nuclear waste continues.

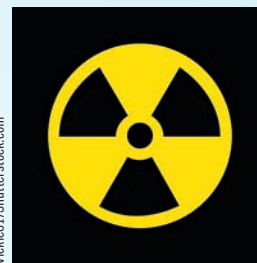
The numbers describing SNF are barely comprehensible to most people. The volume of all existing SNF could cover a large football stadium to a depth of 4 or 5 feet, but no sensible person would want to confine that much heat and radioactivity to one place. There are about 1000 isotopes of about 100 different elements in SNF, and most are radioactive. They decay into stable elements at different rates, giving off alpha, beta, and gamma emissions. It will take about 7000 years until the SNF will be only as radioactive as the rocks and minerals that make up our planet.

These fission products are housed in long titanium rods, each about the diameter of a pencil, that constitute the fuel assembly in a nuclear power plant. Workers wearing gloves can handle fuel assemblies before fissioning occurs. But after removal from a nuclear reactor, the fuel assembly is stored in a cooling pool of water beside the reactor for at least 10 years. On-site storage of the oldest fuel assemblies occurs in specially constructed concrete casks until the federal government takes ownership and finds a suitable place for it.

Other options that have been considered for HLW include outer space ejection and burial in deep ocean trenches. The consensus worldwide is that deep geological isolation is the best option.

For the student who likes a challenge, nuclear waste management is a good one. Here are a few key issues to study and discuss:

- ▶ *Transportation of the waste to its repository.* Should it be done by rail or by truck? Should there be public notification of the time of transport? Are there response measures in place in case of an accident?
- ▶ *The site's seismicity.* Will there be significant volcanic or seismic activity near the site in the next 10,000 years?
- ▶ *Hydrology.* Is there enough evidence to ensure that radionuclides will not seep into groundwater to any significant degree?
- ▶ *Weapons disarmament.* Should the plutonium from "disarmed" nuclear weapons eventually be turned into nuclear fuel or made useless immediately and buried with other HLW?



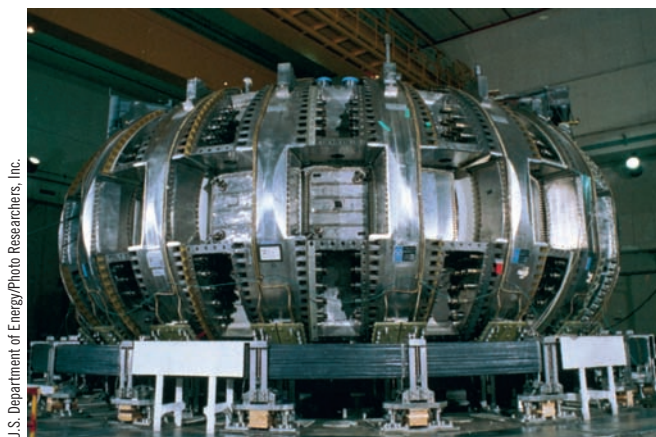
DONALD H. WILLIAMS
HOPE COLLEGE

other stars, but they are nearly impossible to achieve and contain on the earth. Thermonuclear bombs (called fusion bombs or hydrogen bombs) of incredible energy have been detonated in tests but, thankfully, never in war. In them, the necessary activation energy is supplied by the explosion of a fission bomb.

It is hoped that fusion reactions can be harnessed to generate energy for domestic power. Because of the tremendously high temperatures required, no currently known structural material can confine these reactions. At such high temperatures, all molecules dissociate and most atoms ionize, resulting in the formation of a new state of matter called a **plasma**. A very high temperature plasma is so hot that it melts and decomposes anything it touches, including structural components of a reactor. The technological innovation required to build a workable fusion reactor probably represents the greatest challenge ever faced by the scientific and engineering community.

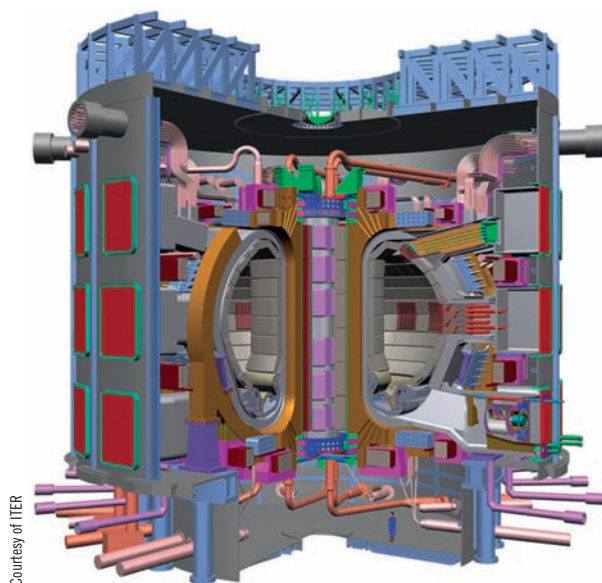
► Plasmas have been called the fourth state of matter.

Recent attempts at the containment of lower-temperature plasmas by external magnetic fields have been successful, and they encourage our hopes. Fusion as a practical energy source, however, lies far in the future at best. The biggest advantages of its use would be that (1) the deuterium fuel can be found in virtually inexhaustible supply in the oceans; and (2) fusion reactions would produce only radionuclides of very short half-life, primarily tritium ($t_{1/2} = 12.3$ years), so there would be no long-term waste disposal problem. If controlled fusion could be brought about, it could liberate us from dependence on uranium and fossil fuels.



U.S. Department of Energy/Photo Researchers, Inc.

The plasma in a fusion reactor must not touch the walls of its vacuum vessel, which would be vaporized. In the Tokamak fusion test reactor, the plasma is contained within a magnetic field shaped like a doughnut. The magnetic field is generated by D-shaped coils around the vacuum vessel.



Courtesy of ITER

Proposed design for a new Tokamak reactor to be built in France. See www.iter.org/.

Unless otherwise noted, all content on this page is © Cengage Learning.

KEY TERMS

Alpha emission Radioactive decay in which an alpha particle is given off from the nucleus.

Alpha particle (α) A particle that consists of two protons and two neutrons; identical to a helium nucleus.

Artificial transmutation An artificially induced nuclear reaction caused by bombardment of a nucleus with subatomic particles or small nuclei.

Band of stability A band containing stable (nonradioactive) nuclides in a plot of number of neutrons versus number of protons (atomic number).

Beta emission Radioactive decay in which an electron is ejected from the nucleus to convert a neutron into a proton.

Beta particle (β) An electron emitted from the nucleus when a neutron decays to a proton and an electron.

Binding energy (nuclear binding energy) The energy equivalent ($E = mc^2$) of the mass deficiency of an atom.

Breeder reactor A fission reactor that produces more fissionable material than it consumes.

Chain reaction A reaction that, once initiated, sustains itself and expands.

Cloud chamber A device for observing the paths of speeding particles as vapor molecules condense on the ionized air molecules in their tracks.

Control rods Rods of materials such as cadmium or boron steel that act as neutron absorbers (not merely moderators), used in nuclear reactors to control neutron fluxes and therefore rates of fission.

Critical mass The minimum mass of a particular fissionable nuclide, in a given volume, that is required to sustain a nuclear chain reaction.

Cyclotron A device for accelerating charged particles along a spiral path.

Daughter nuclide A nuclide that is produced in a nuclear decay.

Electron capture Absorption of an electron from the first energy level (*K shell*) by a proton as it is converted to a neutron; also known as *K capture*; *positron emission*.

Fast neutron A neutron ejected at high kinetic energy in a nuclear reaction.

Fluorescence Absorption of high-energy radiation by a substance and the subsequent emission of visible light.

Gamma ray (γ) High-energy electromagnetic radiation.

Geiger-Müller counter A type of gas ionization counter used to detect radiation.

Half-life of a radionuclide The time required for half of a given sample to undergo radioactive decay.

Heavy water Water containing deuterium, a heavy isotope of hydrogen, ${}^2\text{H}$.

Linear accelerator A device used for accelerating charged particles along a straight-line path.

Mass deficiency (Δm) The amount of matter that would be converted into energy if an atom were formed from constituent particles.

Moderator A substance such as hydrogen, deuterium, oxygen, or paraffin capable of slowing fast neutrons upon collision.

Nuclear binding energy The energy equivalent of the mass deficiency; energy released in the formation of an atom from subatomic particles. See *Binding energy*.

Nuclear fission The process in which a heavy nucleus splits into nuclei of intermediate masses and one or more neutrons are emitted.

Nuclear fusion The combination of light nuclei to produce a heavier nucleus.

Nuclear reaction A reaction involving a change in the composition of a nucleus; it can evolve or absorb an extraordinarily large amount of energy.

Nuclear reactor A system in which controlled nuclear fission reactions generate heat energy on a large scale. The heat energy is subsequently converted into electrical energy.

Nucleons Particles comprising the nucleus; protons and neutrons.

Nuclides Different atomic forms of all elements (in contrast to isotopes, which are different atomic forms of a single element).

Parent nuclide A nuclide that undergoes nuclear decay.

Plasma A physical state of matter that exists at extremely high temperatures, in which all molecules are dissociated and most atoms are ionized.

Positron A nuclear particle with the mass of an electron but opposite charge.

Positron emission See *Electron capture*.

Radiation High-energy particles or rays emitted in nuclear decay processes.

Radioactive dating A method of dating ancient objects by determining the ratio of amounts of a parent nuclide and one of its decay products present in an object and relating the ratio to the object's age via half-life calculations.

Radioactive tracer A small amount of radioisotope that replaces a nonradioactive isotope of the element in a compound whose path (e.g., in the body) or whose decomposition products are to be monitored by detection of radioactivity; also known as a *radiopharmaceutical*.

Radioactivity The spontaneous disintegration of atomic nuclei.

Radioisotope A radioactive isotope of an element.

Radionuclide A radioactive nuclide.

Scintillation counter A device used for the quantitative detection of radiation.

Slow neutron A fast neutron slowed by collision with a moderator.

Thermonuclear energy Energy from nuclear fusion reactions.

Transuranium elements The elements with atomic numbers greater than 92 (uranium); none occur naturally and all must be prepared by nuclear bombardment of other elements.

EXERCISES

● Molecular Reasoning exercises

▲ More Challenging exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Nuclear Stability and Radioactivity

- Define and compare nuclear fission and nuclear fusion. Briefly describe current uses of nuclear fission and fusion.
- Differentiate between natural and induced radioactivity. Use the periodic table to identify the locations of those elements that are the result of induced radioactivity.
- How is a nuclear reaction different from a chemical reaction?
- What is the equation that relates the equivalence of matter and energy? What does each term in this equation represent?
- What is mass deficiency? What is binding energy? How are the two related?
- What are nucleons? What is the relationship between the number of protons and the atomic number? What is the relationship among the number of protons, the number of neutrons, and the mass number?
- Define the term “binding energy per nucleon.” How can this quantity be used to compare the stabilities of nuclei?
- Describe the general shape of the plot of binding energy per nucleon against mass number.
- (a) Briefly describe a plot of the number of neutrons against the atomic number (for the stable nuclides). Interpret the observation that the plot shows a band with a somewhat step-like shape. (b) Describe what is meant by “magic numbers” of nucleons.
- Potassium, $Z = 19$, has a series of naturally occurring isotopes: ^{39}K , ^{40}K , ^{41}K . Identify the isotope(s) of potassium that is/are most likely to be stable and which tend to decay.
- Platinum, $Z = 78$, has a series of naturally occurring isotopes: ^{190}Pt , ^{192}Pt , ^{194}Pt , ^{195}Pt , ^{196}Pt , and ^{198}Pt . Identify the isotope(s) of platinum that is/are most likely to be stable and which tend to decay.
- Indicate the type of emission and the decay product predicted for each unstable isotope listed in Exercise 10.
- Indicate the type of emission and the decay product predicted for each unstable isotope listed in Exercise 11.
- The actual mass of a ^{62}Ni atom is 61.9283 amu. (a) Calculate the mass deficiency in amu/atom and in g/mol for this isotope. (b) What is the nuclear binding energy in kJ/mol for this isotope?
- The actual mass of a ^{108}Pd atom is 107.90389 amu. (a) Calculate the mass deficiency in amu/atom and in g/mol for this isotope. (b) What is the nuclear binding energy in kJ/mol for this isotope?
- Calculate the following for ^{64}Zn (actual mass = 63.9291 amu): (a) mass deficiency in amu/atom; (b) mass deficiency in g/mol; (c) binding energy in J/atom; (d) binding energy in kJ/mol; (e) binding energy in MeV/nucleon.
- Calculate the following for ^{49}Ti (actual mass = 48.94787 amu): (a) mass deficiency in amu/atom; (b) mass deficiency in g/mol; (c) binding energy in J/atom; (d) binding energy in kJ/mol; (e) binding energy in MeV/nucleon.
- Calculate the nuclear binding energy in kJ/mol for each of the following: (a) ^{127}I ; (b) ^{81}Br ; (c) ^{35}Cl . The atomic masses are 126.9044 amu, 80.9163 amu, and 34.96885 amu, respectively.
- Repeat Exercise 18 for (a) ^{36}S , (b) ^{39}K , and (c) ^{24}Mg . Their respective atomic masses are 35.96709 amu, 38.96371 amu, and 23.98504 amu. Which of these nuclides has the greatest binding energy per nucleon?
- Compare the behaviors of α , β , and γ radiation (a) in an electrical field, (b) in a magnetic field, and (c) with respect to ability to penetrate various shielding materials, such as a piece of paper and concrete. What is the composition of each type of radiation?



Geiger-Müller counter

- Why are α -particles that are absorbed internally by the body particularly dangerous?
- Name some radionuclides that have medical uses and list the uses.
- Describe how radionuclides can be used in (a) research, (b) agriculture, and (c) industry.
- Name and describe four methods for detection of radiation.
- Describe how (a) nuclear fission and (b) nuclear fusion generate more stable nuclei.
- What evidence exists to support the theory that nucleons are arranged in “shells” or energy levels within the nucleus?

● Molecular Reasoning exercises

▲ More Challenging exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

Nuclear Reactions

27. Consider a radioactive nuclide with a neutron/proton ratio that is larger than those for the stable isotopes of that element. What mode(s) of decay might be expected for this nuclide? Why?
28. Repeat Exercise 27 for a nuclide with a neutron/proton ratio that is smaller than those for the stable isotopes.
29. Calculate the neutron/proton ratio for each of the following radioactive nuclides, and predict how each of the nuclides might decay: (a) $^{13}_5\text{B}$ (stable mass numbers for B are 10 and 11); (b) $^{92}_{38}\text{Sr}$ (stable mass numbers for Sr are between 84 and 88); (c) $^{192}_{82}\text{Pb}$ (stable mass numbers for Pb are between 204 and 208).
30. What particle is emitted in the following nuclear reactions? Write an equation for each reaction.
- Gold-198 decays to mercury-198.
 - Radon-222 decays to polonium-218.
 - Cesium-137 decays to barium-137.
 - Indium-110 decays to cadmium-110.
31. Write the symbols for the nuclide that is formed in each of the following radioactive decays (β refers to an e^-).
- $^{125}_{50}\text{Sn} \xrightarrow{-\beta}$
 - $^{13}_6\text{C} \xrightarrow{-n}$
 - $^{11}_5\text{B} \xrightarrow{-\gamma}$
 - $^{147}_{62}\text{Sm} \xrightarrow{-\alpha}$
 - $^{184}_{78}\text{Ir} \xrightarrow{-p}$
 - $^{40}_{19}\text{K} \xrightarrow{-\beta}$
32. Predict the kind of decays you would expect for the following radionuclides: (a) $^{60}_{27}\text{Co}$ (n/p ratio too high); (b) $^{20}_{11}\text{Na}$ (n/p ratio too low); (c) $^{222}_{86}\text{Rn}$; (d) $^{67}_{29}\text{Cu}$; (e) $^{238}_{92}\text{U}$; (f) $^{11}_6\text{C}$.
33. There are only four naturally occurring nuclides (out of 263) that have both an odd number of protons and an odd number of neutrons. They are also among the first seven elements and each of them has the same number of neutrons as protons. Give their nuclide symbols.
34. Fill in the missing symbols in the following nuclear bombardment reactions.
- $^{96}_{42}\text{Mo} + ^4_2\text{He} \longrightarrow ^{100}_{43}\text{Tc} + \underline{\hspace{1cm}}$
 - $^{59}_{27}\text{Co} + ^1_0\text{n} \longrightarrow ^{56}_{25}\text{Mn} + \underline{\hspace{1cm}}$
 - $^{23}_{11}\text{Na} + \underline{\hspace{1cm}} \longrightarrow ^{23}_{12}\text{Mg} + ^1_0\text{n}$
 - $^{209}_{83}\text{Bi} + \underline{\hspace{1cm}} \longrightarrow ^{210}_{84}\text{Po} + ^1_0\text{n}$
 - $^{238}_{92}\text{U} + ^{16}_8\text{O} \longrightarrow \underline{\hspace{1cm}} + 5^1_0\text{n}$
35. Fill in the missing symbols in the following nuclear bombardment reactions.
- $^{26}_{12}\text{Mg} + \underline{\hspace{1cm}} \longrightarrow ^{26}_{13}\text{Al} + ^1_0\text{n}$
 - $\underline{\hspace{1cm}} + ^1_1\text{H} \longrightarrow ^{29}_{14}\text{Si} + ^0_0\gamma$
 - $^{232}_{90}\text{Th} + \underline{\hspace{1cm}} \longrightarrow ^{240}_{96}\text{Cm} + 4^1_0\text{n}$
 - $^{40}_{18}\text{Ar} + \underline{\hspace{1cm}} \longrightarrow ^{43}_{19}\text{K} + ^1_1\text{H}$
36. Write the symbols for the daughter nuclides in the following nuclear bombardment reactions: (a) $^{60}_{28}\text{Ni}$ (n, p); (b) $^{98}_{42}\text{Mo}$ ($^1_0\text{n}, \beta$); (c) $^{35}_{17}\text{Cl}$ (p, α).
37. Write the symbols for the daughter nuclides in the following nuclear bombardment reactions: (a) $^{20}_{10}\text{Ne}$ (α, γ); (b) $^{15}_7\text{N}$ (p, α); (c) $^{10}_5\text{B}$ (n, α).
38. Write the nuclear equation for each of the following bombardment processes: (a) $^{14}_7\text{N}$ (α, p) $^{17}_8\text{O}$; (b) $^{106}_{46}\text{Pd}$ (n, p) $^{106}_{45}\text{Rh}$; (c) $^{23}_{11}\text{Na}$ (n, β^-) X. Identify X.
39. Repeat Exercise 38 for the following: (a) $^{113}_{48}\text{Cd}$ (n, γ) $^{114}_{48}\text{Cd}$; (b) ^6_3Li (n, α) ^3_1H ; (c) ^2_1H (γ, p) X. Identify X.
40. Fill in the mass number, atomic number, and symbol for the missing particle in each nuclear equation.
- $^{242}_{94}\text{Pu} \longrightarrow ^4_2\text{He} + \underline{\hspace{1cm}}$
 - $\underline{\hspace{1cm}} \longrightarrow ^{32}_{16}\text{S} + ^0_{-1}\text{e}$
 - $^{252}_{98}\text{Cf} + \underline{\hspace{1cm}} \longrightarrow 3^1_0\text{n} + ^{259}_{103}\text{Lr}$
 - $^{55}_{26}\text{Fe} + \underline{\hspace{1cm}} \longrightarrow ^{55}_{25}\text{Mn}$
 - $^{15}_8\text{O} \longrightarrow \underline{\hspace{1cm}} + ^0_{+1}\text{e}$
41. Summarize the nuclear changes that occur for each of the following types of radioactive emissions by determining the algebraic expressions (using a or z) that would be placed in the boxes for the mass number and the atomic number that would complete the nuclear equation.
- beta: $^a_z\text{X} \longrightarrow \boxed{\hspace{1cm}}\text{Y} + ^0_{-1}\beta$
 positron: $^a_z\text{X} \longrightarrow \boxed{\hspace{1cm}}\text{Y} + ^0_{+1}\beta$
 alpha: $^a_z\text{X} \longrightarrow \boxed{\hspace{1cm}}\text{Y} + ^4_2\alpha$
 proton: $^a_z\text{X} \longrightarrow \boxed{\hspace{1cm}}\text{Y} + ^1_1\text{p}$
 neutron: $^a_z\text{X} \longrightarrow \boxed{\hspace{1cm}}\text{Y} + ^1_0\text{n}$
 gamma: $^a_z\text{X} \longrightarrow \boxed{\hspace{1cm}}\text{Y} + ^0_0\gamma$
42. Write the nuclear equations for the following processes: (a) $^{63}_{28}\text{Ni}$ undergoing β^- emission; (b) two deuterium atoms undergoing fusion to give ^3_2He and a neutron; (c) a nuclide being bombarded by a neutron to form ^7_3Li and an α -particle (identify the unknown nuclide); (d) $^{14}_7\text{N}$ being bombarded by a neutron to form three α -particles and an atom of tritium.
43. Write the nuclear equations for the following processes: (a) $^{226}_{88}\text{Ra}$ undergoing α decay; (b) $^{110}_{49}\text{In}$ undergoing positron emission; (c) $^{127}_{53}\text{I}$ being bombarded by a proton to form $^{121}_{54}\text{Xe}$ and seven neutrons; (d) tritium and deuterium undergoing fusion to form an α -particle and a neutron; (e) $^{95}_{42}\text{Mo}$ being bombarded by a proton to form $^{95}_{43}\text{Tc}$ and radiation (identify this radiation).



Charles D. Winters

Radon test kit

44. "Radioactinium" is produced in the actinium series from $^{235}_{92}\text{U}$ by the successive emission of an α -particle, a β^- -particle, an α -particle, and a β^- -particle. What are the symbol, atomic number, and mass number for "radioactinium"?
45. An alkaline earth element (Group 2A) is radioactive. It undergoes decay by emitting three α -particles in succession. In what periodic table group is the resulting element found?
46. A nuclide of element rutherfordium, $^{257}_{104}\text{Rf}$, is formed by the nuclear reaction of californium-249 and carbon-12, with the emission of four neutrons. This new nuclide rapidly decays by emitting an α -particle. Write the equation for each of these nuclear reactions.
47. Supply the missing information to complete each of the following equations.
- $^{187}_{75}\text{Re} + \beta \longrightarrow ?$
 - $^{243}_{95}\text{Am} + {}^1_0n \longrightarrow {}^{244}_{96}\text{Cm} + ? + \gamma$
 - $^{35}_{17}\text{Cl} + ? \longrightarrow {}^{32}_{16}\text{S} + {}^4_2\text{He}$
 - $^{53}_{24}\text{Cr} + {}^4_2\text{He} \longrightarrow {}^1_0n + ?$
48. Write balanced nuclear equations for:
- the loss of an alpha particle by Th-230
 - the loss of a beta particle by lead-210
 - the fission of U-235 to give Ba-140, another nucleus, and an excess of two neutrons
 - the K-capture of Ar-37.
49. Describe how (a) cyclotrons and (b) linear accelerators work.
59. Analysis of an ant found in a piece of amber provided 14.0 disintegrations of $^{14}_6\text{C}/\text{min} \cdot \text{g C}$, whereas a living ant of the same species produces 16.0 disintegrations per minute per gram of carbon. Calculate the approximate age of the fossilized ant. The half-life of carbon-14 is 5730 years.
60. The practical limit for dating objects by carbon-14 is about 50,000 years because older objects have too little activity to be dated accurately. Given that the half-life of carbon-14 is 5730 years, approximately what fraction of the carbon-14 that was in an object 50,000 years ago is still carbon-14?
61. Strontium-90 is one of the harmful radionuclides that results from nuclear fission explosions. It decays by beta emission with a half-life of 28 years. How long would it take for 99.9% of a given sample released in an atmospheric test of an atomic bomb to disintegrate?
62. Carbon-14 decays by beta emission with a half-life of 5730 years. Assuming a particular object originally contained 8.50 μg of carbon-14 and now contains 0.80 μg of carbon-14, how old is the object?

Fission and Fusion

63. Briefly describe a nuclear fission process. What are the two most important fissionable materials?
64. What is a chain reaction? Why are nuclear fission processes considered chain reactions? What is the critical mass of a fissionable material?
65. Where have continuous nuclear fusion processes been observed? What is the main reaction that occurs in such sources?
66. The reaction that occurred in the first fusion bomb was ${}^7_3\text{Li} (p, \alpha) X$. (a) Write the complete equation for the process, and identify the product, X. (b) The atomic masses are 1.007825 amu for ${}^1_1\text{H}$, 4.00260 amu for α , and 7.01600 amu for ${}^7_3\text{Li}$. Find the energy for the reaction in kJ/mol.
67. Summarize how an atomic bomb works, including how the nuclear explosion is initiated.
68. Discuss the pros and cons of the use of nuclear energy instead of other, more conventional types of energy based on fossil fuels.
69. Describe and illustrate the essential features of a light water fission reactor.
70. How is fissionable uranium-235 separated from nonfissionable uranium-238?
71. Distinguish between moderators and control rods of nuclear reactors.
72. What are the major advantages and disadvantages of fusion as a potential energy source compared with fission? What is the major technological problem that must be solved to permit development of a fusion reactor?
73. ▲ Calculate the binding energy, in kJ/mol of nucleons, for the following isotopes: (a) $^{15}_8\text{O}$ with a mass of 15.00300 amu; (b) $^{16}_8\text{O}$ with a mass of 15.99491 amu; (c) $^{17}_8\text{O}$ with a mass of 16.99913 amu; (d) $^{18}_8\text{O}$ with a mass of 17.99915 amu; (e) $^{19}_9\text{F}$ with a mass of 19.0035 amu. Which of these would you expect to be most stable?
74. ▲ The first nuclear transformation (discovered by Rutherford) can be represented by the shorthand notation

Rates of Decay

50. What does the half-life of a radionuclide represent? How do we compare the relative stabilities of radionuclides in terms of half-lives?
51. Why must all radioactive decays be first order?
52. Describe the process by which steady-state (constant) ratios of carbon-14 to (nonradioactive) carbon-12 are attained in living plants and organisms. Describe the method of radiocarbon dating. What factors limit the use of this method?
53. If the half-life of a radioactive substance is 3.0 hours, how many hours would it take for 99.9% of a sample to decay?
54. The half-life of $^{11}_6\text{C}$ is 20.3 min. How long will it take for 92.5% of a sample to decay? How long will it take for 99.0% of the sample to decay?
55. The activity of a sample of tritium decreased by 5.5% over the period of a year. What is the half-life of ${}^3_1\text{H}$?
56. A very unstable isotope of beryllium, ${}^8\text{Be}$, undergoes emission with a half-life of $0.07 \times 10^{-15} \text{ s}$ (0.07 fs). How long does it take for 99.90% of a 2.0- μg sample of ${}^8\text{Be}$ to undergo decay?
57. The $^{14}_6\text{C}$ activity of an artifact from a burial site was 8.6/min $\cdot \text{g C}$. The half-life of $^{14}_6\text{C}$ is 5730 years, and the current $^{14}_6\text{C}$ activity is 16.1/min $\cdot \text{g C}$ (that is, 16.1 disintegrations per minute per gram of carbon). How old is the artifact?
58. Gold-198 is used in the diagnosis of liver problems. The half-life of ^{198}Au is 2.69 days. If you begin with 2.8 μg of this gold isotope, what mass remains after 10.8 days?



Molecular Reasoning exercises



More Challenging exercises

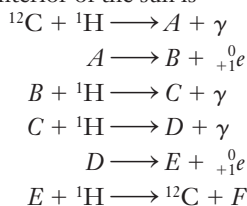
Blue-Numbered

exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

$^{14}_7\text{N}$ (α, p) $^{17}_8\text{O}$. (a) Write the corresponding nuclear equation for this process. The respective atomic masses are 14.00307 amu for $^{14}_7\text{N}$, 4.00260 amu for ^4_2He , 1.007825 amu for ^1_1H , and 16.99913 amu for $^{17}_8\text{O}$. (b) Calculate the energy change of this reaction in kJ/mol.

75. A proposed series of reactions (known as the carbon–nitrogen cycle) that could be important in the very hottest region of the interior of the sun is



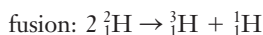
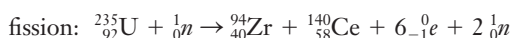
Identify the species labeled A–F.

76. ▲ The ultimate stable product of ^{238}U decay is ^{206}Pb . A certain sample of pitchblende ore was found to contain ^{238}U and ^{206}Pb in the ratio 67.8 atoms ^{238}U :32.2 atoms ^{206}Pb . Assuming that all the ^{206}Pb arose from uranium decay, and that no U or Pb has been lost by weathering, how old is the rock? The half-life of ^{238}U is 4.51×10^9 years.
77. ▲ Calculate the energy released by the fission reaction



The actual masses of the species are, in amu, $^{235}_{92}\text{U}$, 235.0439; $^{90}_{38}\text{Sr}$, 89.8869; $^{144}_{58}\text{Ce}$, 143.8817; 1_0n , 1.0087; $^0_{-1}e$, 0.0005486.

78. ▲ Show by calculation which reaction produces the larger amount of energy per atomic mass unit of material reacting.



The atomic masses are 235.0439 amu for $^{235}_{92}\text{U}$; 93.9061 amu for $^{94}_{40}\text{Zr}$; 139.9053 amu for $^{140}_{58}\text{Ce}$; 3.01605 amu for ^3_1H ; 1.007825 amu for ^1_1H ; 2.0140 amu for ^2_1H ; 1.0087 amu for 1_0n ; 0.0005486 amu for $^0_{-1}e$.

79. ▲ Potassium-40 decays to ^{40}Ar with a half-life of 1.3×10^9 years. What is the age of a lunar rock sample that contains these isotopes in the ratio 33.4 atoms ^{40}K :66.6 atoms ^{40}Ar ? Assume that no argon was originally in the sample and that none has been lost by weathering.

Conceptual Exercises

80. Both nuclear and conventional power plants produce wastes that can be detrimental to the environment. Discuss these wastes and the current problems created by them.
81. If the earth is 4.5×10^9 years old and the amount of radioactivity in a sample becomes smaller with time, how is it possible for there to be any radioactive elements left on the earth that have half-lives of less than a few million years?
82. ● What common type of radioactive emission does not consist of matter?
83. ● How is the process of producing electricity from nuclear fission different from the production of electricity from burning coal?

Building Your Knowledge

84. Why is carbon-14 dating not accurate for estimating the age of material more than 50,000 years old?
85. Polonium-210 decays to Pb-206 by alpha emission. Its half-life is 138 days. What volume of helium at 25°C and 1.20 atm would be obtained from a 25.00-g sample of Po-210 left to decay for 75 hours?

Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

86. Use an internet search engine (such as <http://www.google.com>) to locate information on uranium mining. What two countries produce nearly half of all uranium mined worldwide? What is the most common type of uranium mining? (*Hint*: Is it open pit, leaching, or something else?)
87. Use an internet search engine (such as <http://www.google.com>) to locate information on volatile uranium compounds. Isotopes of uranium are separated by taking advantage of the principle that gases of different masses diffuse at different rates. What is the volatile uranium compound used in the separation of its isotopes? What is “yellow cake”?
88. Open www.woodrow.org/teachers/chemistry/institutes/1992 and under Nuclear Chemistry, click on Frederic Joliot-Curie, or locate a history of science site that describes the life of Frederic Joliot-Curie.
- (a) In addition to being married to each other, what was the relationship between Mme. Curie and Frederic Joliot-Curie?
- (b) What chemical evidence did Frederic Joliot-Curie provide to prove that transmutation had taken place?
89. Open www.energy.gov and enter “fusion” in the search window; go to the “fusion home page” or open a site associated with the U.S. Fusion Energy Sciences Program.
- (a) What is the mission of the U.S. Fusion Energy Sciences Program?
- (b) The U.S. Fusion Energy Sciences Program is a function of which federal department?
90. Use the *Handbook of Chemistry and Physics* to find the decay products and half-lives requested below.
- (a) Cm-244 decays in three steps, each emitting an alpha particle, to yield Th-232. Write the equation for each decay step.
- (b) What is the half-life of each product formed?
- (c) What is the half-life of Cm-244?
91. A full-page version of the Radon Zone Map is available at the EPA radon web site, <http://www.epa.gov/radon/zonemap.html>. What are the predicted average indoor radon levels for the counties where your college and home are located? If the numbers are low, does this mean you do not need to worry about radon exposure?

Organic Chemistry I: Formulas, Names, and Properties

23



Waxes are high-molecular-weight straight-chain alkanes, alcohols, and carboxylic acids.

Charles D. Winters

OUTLINE

Saturated Hydrocarbons

- 23-1 Alkanes and Cycloalkanes
- 23-2 Naming Saturated Hydrocarbons

Unsaturated Hydrocarbons

- 23-3 Alkenes
- 23-4 Alkynes

Aromatic Hydrocarbons

- 23-5 Benzene
- 23-6 Other Aromatic Hydrocarbons
- 23-7 Hydrocarbons: A Summary

Functional Groups

- 23-8 Organic Halides
- 23-9 Alcohols and Phenols
- 23-10 Ethers
- 23-11 Aldehydes and Ketones
- 23-12 Amines
- 23-13 Carboxylic Acids
- 23-14 Some Derivatives of Carboxylic Acids
- 23-15 Summary of Functional Groups

Fundamental Classes of Organic Reactions

- 23-16 Substitution Reactions
- 23-17 Addition Reactions
- 23-18 Elimination Reactions
- 23-19 Polymerization Reactions

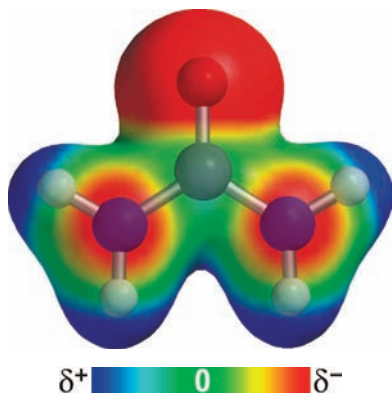
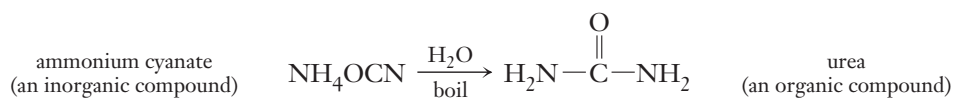
OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Describe saturated hydrocarbons (alkanes and cycloalkanes)—their structures and their nomenclature
- ▶ Describe unsaturated hydrocarbons (alkenes and alkynes)—their structures and their nomenclature
- ▶ Draw and name constitutional isomers of alkanes
- ▶ Draw and name constitutional and geometric isomers of alkenes
- ▶ Describe and name some aromatic hydrocarbons—benzene, condensed aromatics, and substituted aromatic compounds
- ▶ Describe some common functional groups and name compounds from the following classes
 - halides
 - alcohols and phenols
 - ethers
 - aldehydes and ketones
 - amines
 - carboxylic acids and some of their derivatives
- ▶ Recognize examples of the four fundamental classes of organic reactions: substitution, addition, elimination, and polymerization
- ▶ Describe some uses of the four fundamental classes of organic reactions and some compounds that are prepared by each class of reaction
- ▶ Recognize some common polymers and the reactions by which they are formed; identify the monomers from which they are formed

Organic chemistry is the study of carbon-containing compounds that contain C — C or C — H bonds, and sometimes a few other elements such as oxygen, nitrogen, sulfur, phosphorus, and the halogens. Why is one entire branch of chemistry devoted to the behavior of the compounds of just one element? The answer is twofold: (1) There are many more compounds that contain carbon than there are compounds that do not (more than 20 million organic compounds have been identified), and (2) the molecules containing carbon can be so much larger and more complex (a methane molecule contains five atoms per molecule and DNA contains tens of billions of atoms per molecule).

Originally the term “organic” was used to describe compounds of plant or animal origin. “Inorganic” was used to describe compounds from minerals. In 1828, Friedrich Wöhler (1800–1882) synthesized urea by boiling ammonium cyanate with water.



Urea, $\text{H}_2\text{N}-\text{CO}-\text{NH}_2$, is the principal end product of metabolism of nitrogen-containing compounds in mammals. It is eliminated in the urine. An adult man excretes about 30 grams of urea in 24 hours.

This disproved the theory that held that organic compounds could be made only by living things. Today many organic compounds are manufactured from inorganic materials.

We encounter organic chemistry in every aspect of our lives. All life is based on a complex interrelationship of thousands of organic substances—from simple compounds such as sugars, amino acids, and fats to vastly more complex ones such as the enzymes that catalyze life’s chemical reactions and the huge DNA molecules that carry genetic information from one generation to the next. The food we eat (including many additives); the clothes we wear; the plastics and polymers that are everywhere; our life-saving medicines; the paper on which we write; our fuels; many of our poisons, pesticides, dyes, soaps, and detergents—all involve organic chemistry.

Most people think of petroleum and natural gas as fuel sources, but most synthetic organic materials are also derived from these two sources. More than half of the top 50 commercial chemicals are organic compounds derived in this way. Indeed, petroleum and natural gas may one day be more valuable as raw materials for organic synthesis than as fuel sources. If so, we may greatly regret our delay in developing alternative energy sources while burning up vast amounts of our petroleum and natural gas deposits as fuels.

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 23-1 Hybridization of Carbon in Covalent Bond Formation

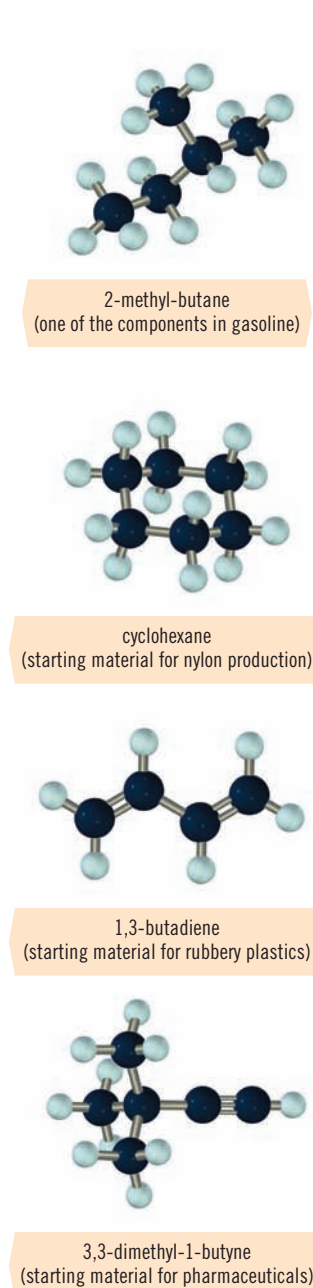
Hybridization and Resulting Geometry	Orbitals Used by Each C Atom	Bonds Formed by Each C Atom	Example
sp^3 , tetrahedral	four sp^3 hybrids	four σ bonds	ethane
sp^2 , trigonal planar	three sp^2 hybrids, one p orbital	three σ bonds, one π bond	ethylene
sp , linear	two sp hybrids, two p orbitals	two σ bonds, two π bonds	acetylene

A carbon atom has four electrons in its outermost shell with ground state configuration $1s^2 2s^2 2p^2$. The C atom can attain a stable configuration by forming four covalent bonds. As we saw in Chapter 8, each C atom can form single, double, or triple bonds by utilizing various hybridizations. The bonding of carbon is summarized in Table 23-1 using examples that we saw in Chapters 7 and 8. Carbon is unique among the elements in the extent to which it forms bonds between like atoms and in the diversity of compounds that are formed. Bonds between atoms of the same element rarely occur for any element except carbon. Carbon atoms form long chains, branched chains, and rings that may also have chains attached to them. A tremendous variety of carbon-containing compounds is known.

Although millions of organic compounds are known, the elements they contain are very few: C and H; often N, O, S, P, or a halogen; and sometimes another element. The great number and variety of organic compounds result from the many different *structures*, or arrangements of atoms, that are possible. The chemical and physical properties of organic compounds depend on the structures of their molecules. Thus, an understanding of structure and bonding is the basis for organizing and understanding organic chemistry.

In this text, we shall give only an introduction to organic chemistry. We will organize organic compounds into the most common classes or “families” according to their structural features and learn to name various types of compounds. In this chapter and the next, we will present a few typical reactions of organic substances.

Organic molecules are based on a framework of carbon–carbon and carbon–hydrogen bonds. Many compounds contain *only* the two elements C and H; these compounds are



► The term “saturated” comes from early studies in which chemists tried to add hydrogen to various organic substances. Those to which no more hydrogen could be added were called saturated, by analogy with saturated solutions.

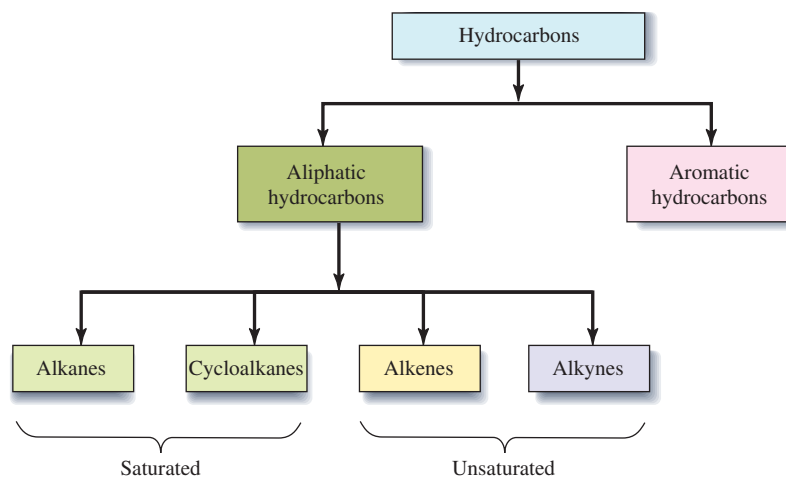


Figure 23-1 Classification of hydrocarbons.

called **hydrocarbons**. Hydrocarbons that contain a delocalized ring of pi bonds such as the benzene ring (see Section 9-6) are called **aromatic hydrocarbons**. Those that do not contain such delocalized systems are called **aliphatic hydrocarbons**. Aliphatic hydrocarbons that contain only sigma (σ) bonds (i.e., only single bonds) are called **saturated hydrocarbons**. Those that contain both sigma and pi (π) bonds (i.e., double, triple, or delocalized bonds) are called **unsaturated hydrocarbons**. These classifications are diagrammed in Figure 23-1. The first seven sections of this chapter are devoted to the study of hydrocarbons.

A **functional group** is a special arrangement of atoms within an organic molecule that is responsible for some characteristic chemical behavior (reactions) of the compound. Different molecules that contain the same functional groups have similar chemical behavior. We shall follow the study of hydrocarbons with a presentation of some important characteristic functional groups.

Saturated Hydrocarbons

23-1 Alkanes and Cycloalkanes

The *saturated hydrocarbons*, or **alkanes**, are compounds in which each carbon atom is bonded to four other atoms. **Cycloalkanes** are saturated hydrocarbons that contain carbon atoms joined to form a ring.

Each H atom in a hydrocarbon is bonded to only one C atom. Saturated hydrocarbons contain only single bonds. Petroleum and natural gas are composed mostly of saturated hydrocarbons.

Alkanes

In Section 8-7, we examined the structure of the simplest alkane, *methane*, CH_4 . We saw that methane molecules are tetrahedral with sp^3 hybridization at carbon (Figure 23-2).

Ethane, C_2H_6 , is the next simplest saturated hydrocarbon. Its structure is quite similar to that of methane. Two carbon atoms share a pair of electrons. Each carbon atom also shares an electron pair with each of three hydrogen atoms. Both carbon atoms are sp^3 hybridized (Figure 23-3). *Propane*, C_3H_8 , is the next member of the family (Figure 23-4).

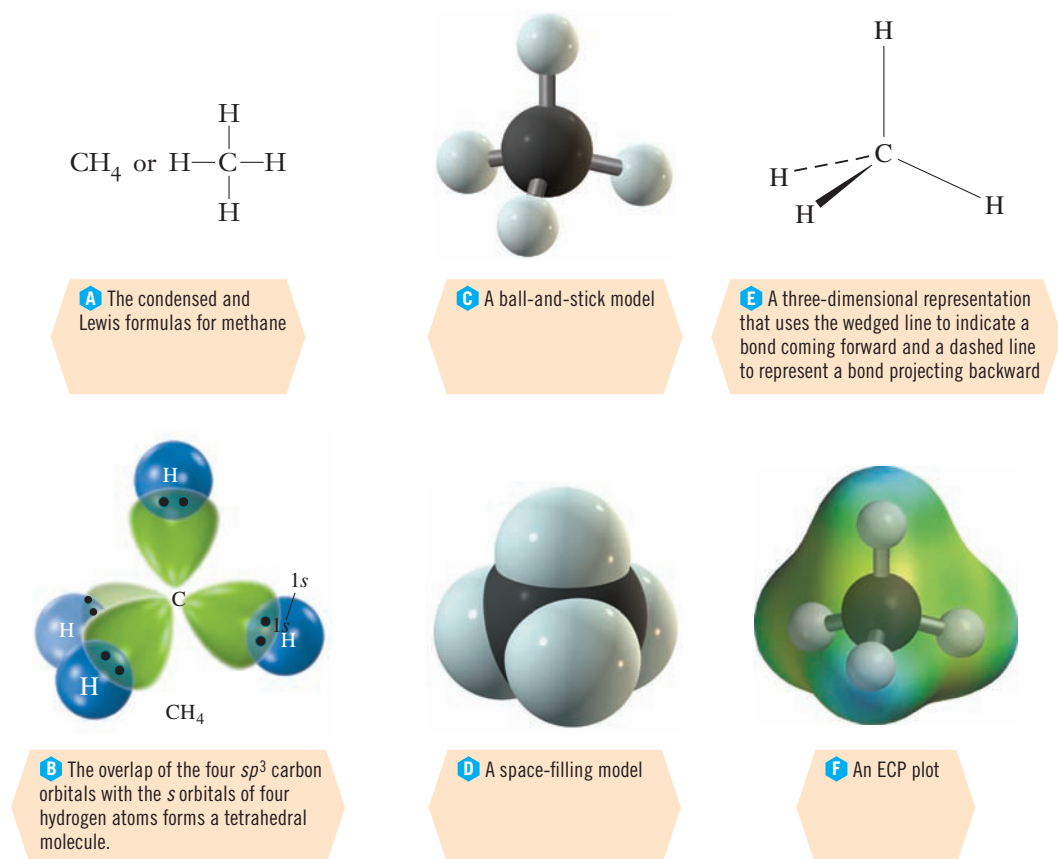


Figure 23-2 Representations of a molecule of methane, CH_4 .

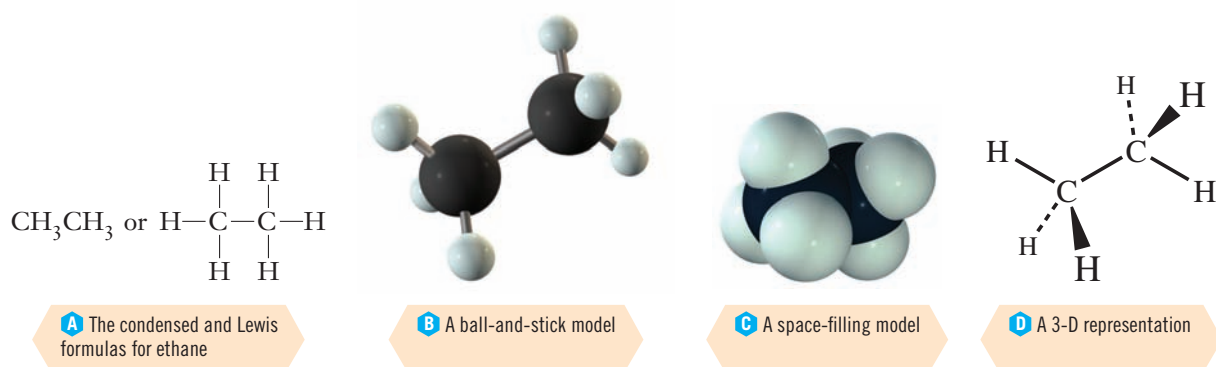


Figure 23-3 Models of ethane, C_2H_6 .

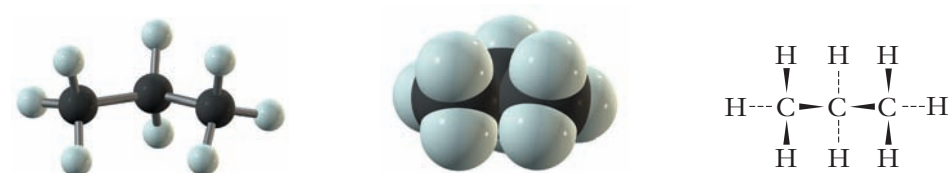
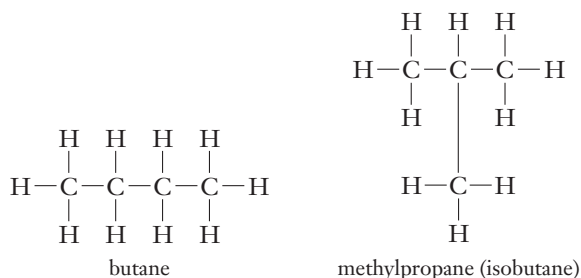


Figure 23-4 Ball-and-stick and space-filling models and a three-dimensional representation of propane, C_3H_8 .

There are two different compounds with the formula C_4H_{10} but different structures. Hence they have different properties. These two C_4H_{10} structures are:



Ball-and-stick models of these two C_4H_{10} alkanes are shown in Figure 23-5. The model in part (a) shows butane, which has all four carbon atoms in a single chain with no branching. Because it has no branching, it is called a “straight-chain” hydrocarbon. Though somewhat misleading, the term “straight-chain” is widely used. The carbon chain is linear only in the structural formulas that we write. Such chains are actually zigzag due to the tetrahedral bond angles at each carbon and are sometimes further kinked or twisted. Think of such a chain of carbon atoms as “continuous.” We can trace a single path from one end of the carbon chain (the terminal carbon) to the other and pass through every other C atom *without backtracking*.

In model (b), the longest chain that can be traced contains only *three* C atoms; the fourth carbon atom is attached to the side of the three-carbon chain to form a *branched-chain* arrangement of the four carbons. This is the simplest branched-chain hydrocarbon.

The formulas of the alkanes, whether straight-chain or branched-chain, can be written in general terms as C_nH_{2n+2} , where n is the number of carbon atoms per molecule. The first five members of the series are

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
Number of C atoms = n	1	2	3	4	5
Number of H atoms = $2n + 2$	4	6	8	10	12

► This hydrocarbon is sometimes called by the simple name isobutane. In Section 23-2, we will learn a more systematic method for naming organic compounds.

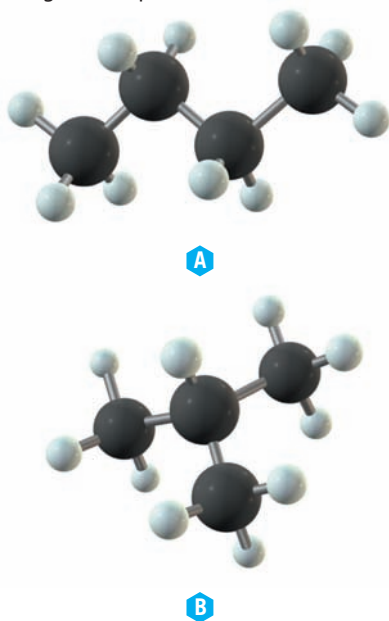


Figure 23-5 Ball-and-stick models of the two isomeric C_4H_{10} hydrocarbons, butane, $CH_3CH_2CH_2CH_3$, and isobutane (methylpropane), CH_3CHCH_3
 $\quad \quad \quad |$
 $\quad \quad \quad CH_3$.

The formula of each alkane differs from the next by CH_2 , a *methylene group*.

A series of compounds in which each member differs from the next by a specific number and kind of atoms is called a **homologous series**. The properties of members of such a series are closely related. The boiling points of the lighter members of the straight-chain saturated hydrocarbon series are shown in Figure 23-6. As the molecular weights of the straight-chain hydrocarbons increase, their boiling points also increase regularly. Properties such as boiling point depend on the forces between molecules (see Chapter 13). Carbon-carbon and carbon-hydrogen bonds are essentially nonpolar and are arranged tetrahedrally around each C atom. As a result, saturated hydrocarbons are nonpolar molecules, and the only significant intermolecular forces are dispersion forces (see Section 13-2). These forces, which are due to induced dipoles, become stronger as the sizes of the molecules and the number of electrons in each molecule increase. Thus, trends such as those depicted in Figure 23-6 are due to the increase in effectiveness of dispersion forces.

Some systematic method for naming compounds is necessary. The system in use today is prescribed by the International Union of Pure and Applied Chemistry (IUPAC). The names of the first 20 straight-chain alkanes are listed in Table 23-2. You should become familiar with at least the first ten. The names of the alkanes starting with pentane have prefixes (from Greek) that give the number of carbon atoms in the molecules. All alkane names have the *-ane* ending.

We have seen that there are two different C_4H_{10} molecules. These different molecules are called *isomers*.

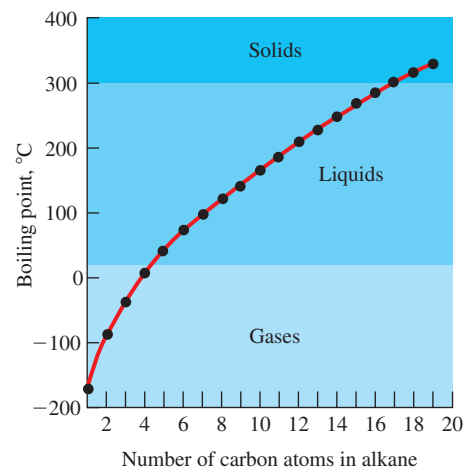
Two different compounds that have the same formula are called **isomers**.

► From the Greek: iso = “same”; mer = “part.” The word *isomer* means “same parts.”

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 23-2 Some Straight-Chain Hydrocarbons (Alkanes)

Molecular Formula	IUPAC Name	Normal bp (°C)	Normal mp (°C)	State at Room Temperature
CH ₄	methane	-161	-184	gas
C ₂ H ₆	ethane	-88	-183	
C ₃ H ₈	propane	-42	-188	
C ₄ H ₁₀	butane	+0.6	-138	
C ₅ H ₁₂	pentane	36	-130	liquid
C ₆ H ₁₄	hexane	69	-94	
C ₇ H ₁₆	heptane	98	-91	
C ₈ H ₁₈	octane	126	-57	
C ₉ H ₂₀	nonane	150	-54	
C ₁₀ H ₂₂	decane	174	-30	
C ₁₁ H ₂₄	undecane	194.5	-25.6	
C ₁₂ H ₂₆	dodecane	214.5	-9.6	
C ₁₃ H ₂₈	tridecane	234	-6.2	
C ₁₄ H ₃₀	tetradecane	252.5	+5.5	
C ₁₅ H ₃₂	pentadecane	270.5	10	
C ₁₆ H ₃₄	hexadecane	287.5	18	solid
C ₁₇ H ₃₆	heptadecane	303	22.5	
C ₁₈ H ₃₈	octadecane	317	28	
C ₁₉ H ₄₀	nonadecane	330	32	
C ₂₀ H ₄₂	eicosane	205 (at 15 torr)	36.7	

**Figure 23-6** A plot of normal boiling point versus the number of carbon atoms in straight-chain, saturated hydrocarbons.

Isomers of this type are known as *constitutional isomers*.

Constitutional isomers (formerly called *structural isomers*) have the *same* molecular formula but *differ in the order* in which their atoms are attached.

For the C₅ alkanes, the atoms can be arranged in three possible orders. These three different C₅H₁₂ alkanes are thus also constitutional isomers. There are five constitutional isomers of C₆H₁₄ (Table 23-3).

In one kind of constitutional isomer, known as the *positional isomer*, the compounds have the same number and kinds of groups on the same base chain or the same ring, but *in different positions*. The last two hexanes shown in Table 23-3 are positional isomers of one another. Note that they both contain a basic saturated four-carbon chain (butane) but they have methyl (—CH₃) groups at different positions along that chain. As we will see in Section 23-2, this determines how we assign their names.

The number of constitutional isomers increases rapidly as the number of carbon atoms in saturated hydrocarbons increases. Table 23-4 displays the number of isomers of some saturated hydrocarbons (alkanes). Most of these isomers have not been prepared or isolated. They probably never will be!

As the degree of branching increases for a series of molecules of the same molecular weight, the molecules become more compact. A compact molecule can have fewer points of contact with its neighbors than more extended molecules do. As a result, attractions due to the total induced dipole forces (dispersion forces) are weaker for branched molecules, and the boiling points of such compounds are lower. This pattern can be seen in the data in Table 23-3 and in Example 23-1.

► Rotation about a single bond does *not* generate a different isomer. For example, the following two drawings differ only by rotation about the bond shown in red; they both represent the same isomer of C₅H₁₂ (see Example 23-1).

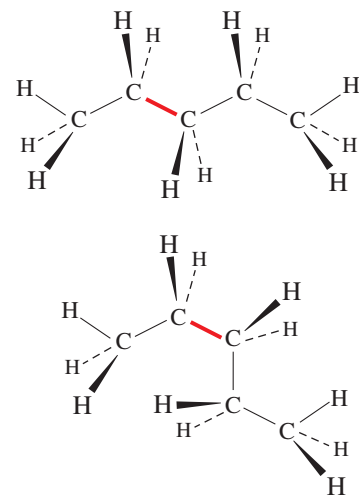
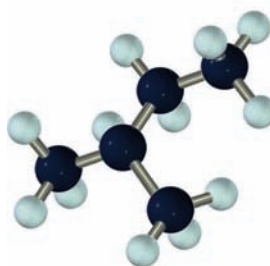


Table 23-4 Numbers of Possible Constitutional Isomers of Alkanes

Formula	Isomers
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{11}H_{24}$	159
$C_{12}H_{26}$	355
$C_{13}H_{28}$	802
$C_{14}H_{30}$	1,858
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	366,319
$C_{25}H_{52}$	36,797,588
$C_{30}H_{62}$	4,111,846,763



$CH_3CH_2CH_2CH_2CH_3$, $CH_3C(CH_3)_3$, and $CH_3CH_2CH(CH_3)_2$.

Table 23-3 Isomeric C_6H_{14} Alkanes

IUPAC Name	Formula	Normal bp ($^{\circ}C$)
hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	68.7
2-methylpentane	$CH_3CH_2CH_2CH(CH_3)CH_3$	60.3
3-methylpentane	$CH_3CH_2CH(CH_3)CH_2CH_3$	63.3
2,2-dimethylbutane	$CH_3CH_2C(CH_3)_2CH_3$	49.7
2,3-dimethylbutane	$CH_3CH(CH_3)CH(CH_3)CH_3$	58.0

EXAMPLE 23-1 Isomeric Alkanes

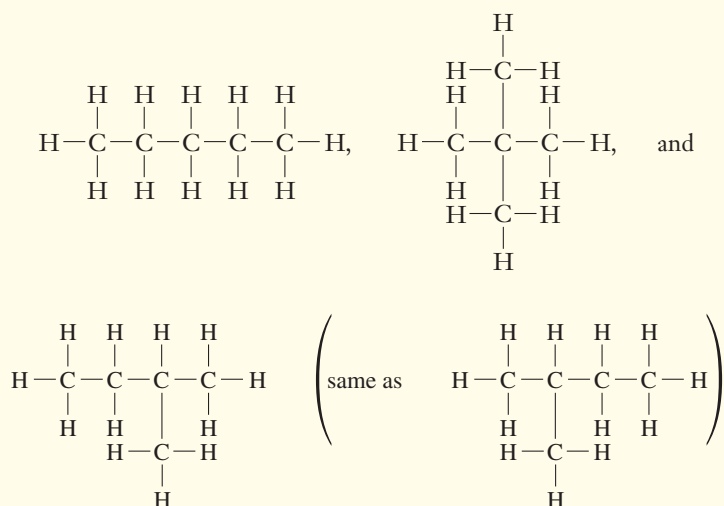
Write the Lewis formula of each of the three isomers having the molecular formula of C_5H_{12} . The boiling points of the three isomers are $9.5^{\circ}C$, $27.9^{\circ}C$, and $36.1^{\circ}C$. Match each compound with its boiling point.

Plan

We first write the carbon skeleton of the straight-chain isomer (no branching). Then we remove one carbon from the straight-chain structure and reposition it to form the skeleton for a branched isomer. We check to see whether branching is possible at other carbon atoms. Then we remove a second carbon and, if possible, form additional branching, and so on. Finally, we add hydrogen atoms to each skeleton to complete the structure.

Solution

The three compounds are:



The compound with the most branching would be expected to be the one with the lowest boiling point, and the straight-chain isomer would be expected to have the highest boiling point.

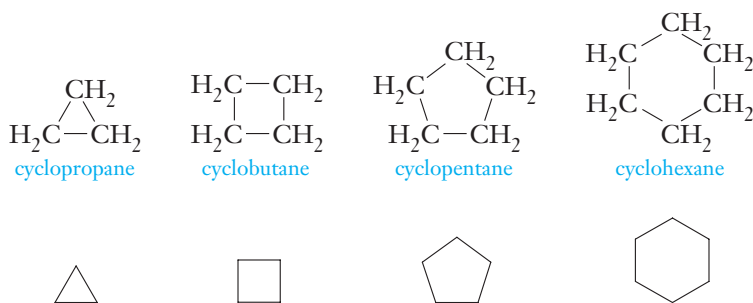
$\text{CH}_3\text{C}(\text{CH}_3)_3$, bp = 9.5°C ; $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2$, bp = 27.9°C ;
and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, bp = 36.1°C .

(Models of these compounds are shown in the margin.)

You should now work Exercise 15.

Cycloalkanes

The cyclic saturated hydrocarbons, or *cycloalkanes*, have the general formula C_nH_{2n} . The cycloalkanes (and other compounds that we will encounter later) are often shown in simplified skeletal form in which each intersection of lines represents a C atom; we mentally add enough H atoms to give each carbon atom four bonds. The first four unsubstituted cycloalkanes and their simplified representations are



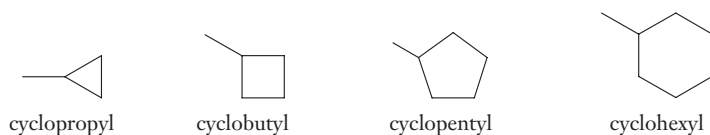
In some of these structures, the bond angles are somewhat distorted from the ideal tetrahedral angle of 109.5° , the most severe distortions being 60° in cyclopropane and 90° in cyclobutane. As a result, these rings are said to be “strained,” and these two compounds are unusually reactive for saturated hydrocarbons. Cyclopentane is stable with a nearly flat ring, because the bond angles in a regular pentagon (108°) are near the tetrahedral angle (109.5°).

Cyclohexane is not stable as a flat ring. The bond angles of the flat ring would be 120° , far from the 109.5° of an sp^3 -hybridized carbon. To avoid the strain that would result, the ring “puckers” and becomes nonplanar (Figure 23-7).

23-2 Naming Saturated Hydrocarbons

It is important to realize that many compounds (and their names) were so familiar to chemists before the development of the IUPAC system (beginning about 1890) that they continued to be called by their common, or “trivial,” names. In this and the next chapter, IUPAC names of compounds appear in blue type, and alternative names are shown in black type.

The IUPAC naming system is based on the names of unbranched hydrocarbons as given in Table 23-2. To name a branched-chain hydrocarbon, we first find the longest chain of carbon atoms and use the root name that corresponds to that hydrocarbon. We then indicate the positions and kinds of *substituents* attached to the chain. **Alkyl group** substituents attached to the longest chain are thought of as fragments of hydrocarbon molecules obtained by the removal of one hydrogen atom. We give them names related to the parent hydrocarbons from which they are derived. Other alkyl groups are named similarly (Table 23-5). We use the general symbol R to represent any alkyl group. The cycloalkyl groups derived from the first four cycloalkanes are called cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl, respectively.



► Noncyclic compounds are sometimes referred to as acyclic compounds.

► In skeletal representations, each intersection represents a carbon with any attached hydrogens. (See Section 23-3 for more details on writing skeletal representations.)

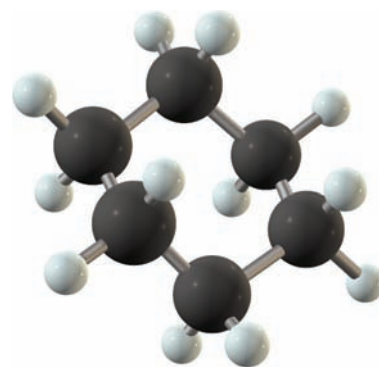


Figure 23-7 A model showing a nonplanar arrangement of cyclohexane.

Table 23-5 Some Alkanes and Their Related Alkyl Groups

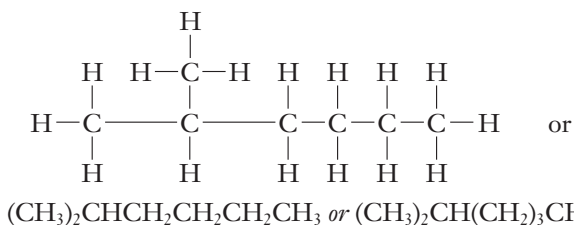
Parent Hydrocarbon	Alkyl group, —R	
CH ₄ , methane $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$ or CH ₄	—CH ₃ , methyl $\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{H} \\ \\ \text{H} \end{array}$ or —CH ₃	
C ₂ H ₆ , ethane $\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$ or CH ₃ CH ₃	—C ₂ H ₅ , ethyl $\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$ or —CH ₂ CH ₃	
C ₃ H ₈ , propane $\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & \\ \text{H} & \text{H} & \text{H} \end{array}$ or CH ₃ CH ₂ CH ₃	—C ₃ H ₇ , propyl $\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\ & & \\ -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & \\ \text{H} & \text{H} & \text{H} \end{array}$ or —CH ₂ CH ₂ CH ₃	—C ₃ H ₇ , isopropyl $\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & \\ \text{H} & & \text{H} \end{array}$
C ₄ H ₁₀ , butane $\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$ or CH ₃ (CH ₂) ₂ CH ₃	—C ₄ H ₉ , butyl $\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$ or —CH ₂ (CH ₂) ₂ CH ₃	—C ₄ H ₉ , <i>sec</i> -butyl (read as “secondary butyl”) $\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & \\ \text{H} & & \text{H} & \text{H} \end{array}$
C ₄ H ₁₀ , methylpropane (common name, isobutane) $\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ or CH(CH ₃) ₃	—C ₄ H ₉ , <i>t</i> -butyl (read as “tertiary butyl”) $\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ or —C(CH ₃) ₃	—C ₄ H ₉ , isobutyl $\begin{array}{c} -\text{CH}_2 \\ \\ \text{H}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$

► Formerly the rule was to name the substituents in order of increasing complexity. This was sometimes difficult to determine. With the use of computers in literature searches, it became necessary to adopt the more definitive alphabetization of the names of substituents.

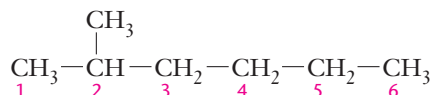
SUMMARY OF IUPAC RULES FOR NAMING ALKANES

1. Find the longest chain of C atoms. Choose the base name that describes the number of C atoms in this chain, with the ending *-ane* (Table 23-2). The longest chain may not be obvious at first if branches of different sizes are present.
2. Number the C atoms in this longest chain beginning at the end nearest the first branching. If necessary, go to the second branch closest to an end, and so on, until a difference is located. If there is branching at equal distances from both ends of the longest chain, begin numbering at the end nearest the branch that is first in alphabetical order.
3. Assign the name and position number to each substituent. Arrange the substituents in alphabetical order. Hyphenated prefixes, such as *tert*- and *sec*-, are not used in alphabetization of the substituents.
4. Use the appropriate prefix to group like substituents: di- = 2, tri- = 3, tetra- = 4, penta- = 5, and so on. Don't consider these prefixes when alphabetizing attached groups.
5. Write the name as a single word. Use hyphens to separate numbers and letters (plus some hyphenated prefixes) and commas to separate numbers. Don't leave any spaces.

Let's name the following compound.



We follow Rules 1 and 2 to number the carbon atoms in the longest chain.



The methyl group is attached to the *second* carbon atom in a *six-carbon* chain, so the compound is named 2-methylhexane.

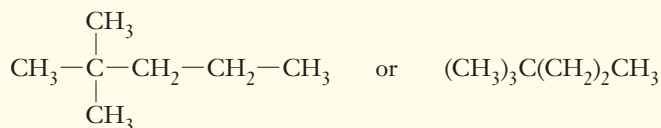
The following examples further illustrate the rules of nomenclature.

► Parentheses are used to conserve space. Formulas written with parentheses must indicate unambiguously the structure of the compound. The parentheses here indicate that the CH_3 group is attached to the C next to it.

► It is incorrect to name the compound 5-methylhexane because that violates Rule 2.

EXAMPLE 23-2 Naming Alkanes

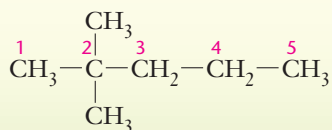
Give the IUPAC name of the compound represented by the structural formula



Plan

We first find the longest carbon chain and number it to give the substituent encountered first the smallest possible number. Then we name the substituents as in Table 23-5 and specify the number of each as indicated in Rule 4.

Solution

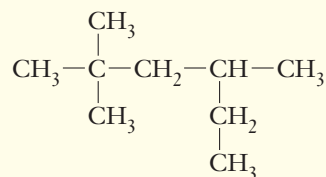


The longest chain contains five carbons, so this compound is named as a derivative of pentane. There are two methyl groups, both at carbon number 2. The IUPAC name of this compound is **2,2-dimethylpentane**.

► Remember that the (dash) formulas indicate which atoms are bonded to each other. They do *not* show molecular geometry. In this molecule, each C atom is tetrahedrally bonded to four other atoms.

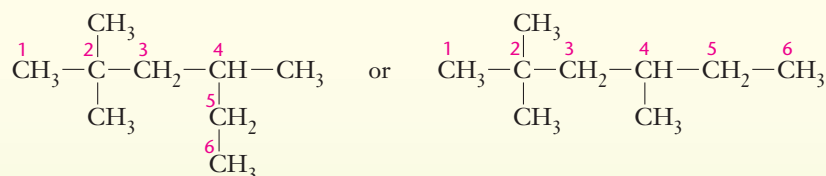
EXAMPLE 23-3 Naming Alkanes

Give the IUPAC name of the compound represented by the structural formula



Plan

The approach is the same as in Example 23-2. We should be aware that the longest carbon chain might not be *written* in a straight line.

Solution

(rewritten to emphasize the six-C chain)

The longest chain contains six carbons, so this compound is named as a derivative of hexane. There are three methyl substituents: two at carbon number 2 and one at carbon number 4. The IUPAC name of this compound is **2,2,4-trimethylhexane**.

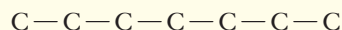
You should now work Exercises 13 and 14.

EXAMPLE 23-4 Writing Formulas from Names

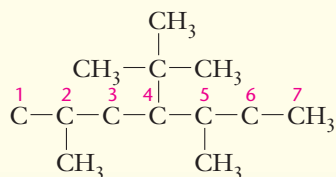
Write the structure for 4-*tert*-butyl-2,5-dimethylheptane.

Plan

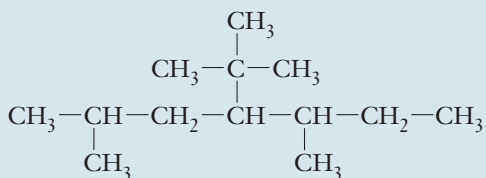
The root name “heptane” indicates that there is a saturated seven-carbon chain.



The names and numbers of the substituents tell us where to attach the alkyl groups.

Solution

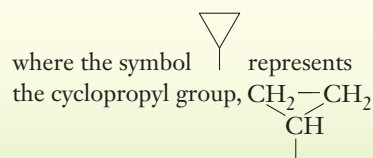
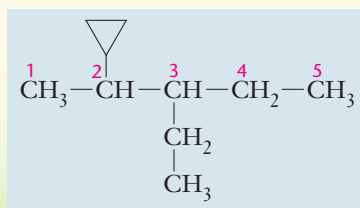
Then we fill in enough hydrogens to saturate each C atom and arrive at the structure

**EXAMPLE 23-5 Writing Formulas from Names**

Write the structure for the compound 2-cyclopropyl-3-ethylpentane.

Plan

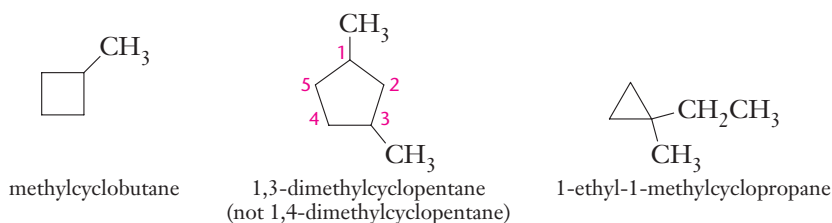
The root name “pentane” tells us that the structure is based on a saturated five-carbon chain. We place the substituents at the positions indicated by the numbers in the name.

Solution

You should now work Exercise 16.

► Recall that the cycloalkanes may also be represented by the general formula C_nH_{2n} .

The names of substituted cycloalkanes are derived analogously to those of alkanes. (1) The base name is determined by the number of carbon atoms in the ring using the same base name as the alkane with the addition of *cyclo* in front. (2) If only one substituent is attached to the ring, no “location number” is required because all positions in a cycloalkane are equivalent. (3) Two or more functional groups on the ring are identified by location numbers, which should be assigned sequentially to the ring carbons in the order that gives the *smallest sum* of location numbers.



► 1,3-dimethylcyclopentane can exist as two different isomers: one with both methyl groups on the same side of the ring (*cis*-), the other with the methyl groups on opposite sides of the plane of the ring (*trans*-). (See Section 23-3.)

Unsaturated Hydrocarbons

There are three classes of unsaturated hydrocarbons: (1) the alkenes and their cyclic counterparts, the cycloalkenes; (2) the alkynes and the cycloalkynes; and (3) the aromatic hydrocarbons.

23-3 Alkenes

The simplest **alkenes** contain one carbon–carbon double bond, $\text{C}=\text{C}$, per molecule. The general formula for noncyclic alkenes is C_nH_{2n} . The smallest alkene is C_2H_4 , ethene, which is usually called by its common name, ethylene.

The bonding in ethylene (Figure 23-8) was described in Section 8-14. The hybridization (sp^2) and bonding at other double-bonded carbon atoms are similar. Both carbon atoms in C_2H_4 are located at the centers of trigonal planes. Rotation about $\text{C}=\text{C}$ double bonds does not occur significantly at room temperature. Compounds that have the general formula $(\text{XY})\text{C}=\text{C}(\text{XY})$ therefore exist as a pair of *cis-trans* isomers. Figure 23-9 shows the *cis-trans* isomers of 1,2-dichloroethene. The existence of compounds with different arrangements of groups on the opposite sides of a bond with restricted rotation is called **geometric isomerism**. This *cis-trans* isomerism can occur across double bonds in alkenes and across single bonds in rings.

Two shared electron pairs draw the atoms closer together than a single electron pair does. Thus, carbon–carbon double bonds are shorter than $\text{C}-\text{C}$ single bonds, 1.34 Å versus 1.54 Å. The physical properties of the alkenes are similar to those of the alkanes, but their chemical properties are quite different.

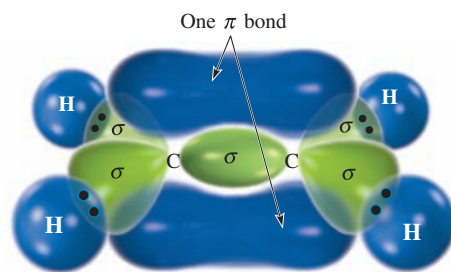


Figure 23-8 Four $\text{C}-\text{H}$ σ bonds, one $\text{C}-\text{C}$ σ bond (green), and one $\text{C}-\text{C}$ π bond (blue) on the planar C_2H_4 molecule.

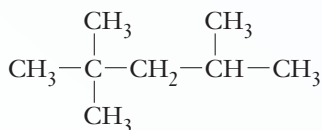
CHEMISTRY IN USE

Petroleum

Petroleum, or crude oil, was discovered in the United States (Pennsylvania) in 1859 and in the Middle East (Iran) in 1908. It has been found in many other locations since these initial discoveries and is now pumped from the ground in many parts of the world. Petroleum consists mainly of hydrocarbons. Small amounts of organic compounds containing nitrogen, sulfur, and oxygen are also present. Each oil field produces petroleum with a particular set of characteristics. Distillation of petroleum produces several fractions.

Gasoline is much in demand, so higher hydrocarbons (C_{12} and up) are “cracked” to increase the amount of gasoline that can be made from a barrel of petroleum. The hydrocarbons are heated, in the absence of air and in the presence of a catalyst, to produce a mixture of smaller alkanes that can be used in gasoline. This process is called *catalytic cracking*.

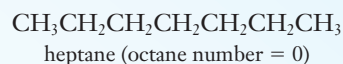
The *octane number* (rating) of a gasoline indicates how smoothly it burns and how much engine “knock” it produces. (Engine knock is caused by premature detonation of fuel in the combustion chamber.) 2,2,4-Trimethylpentane, isooctane, has excellent combustion properties and was arbitrarily assigned an octane number of 100. Heptane, $CH_3(CH_2)_5CH_3$, has very poor combustion properties and was assigned an octane number of zero.



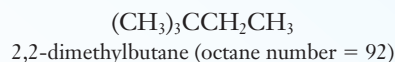
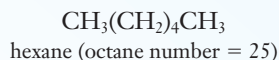
isooctane (octane number = 100)



Petroleum refinery towers.



Mixtures of these two were prepared and burned in test engines to establish the octane scale. The octane number of such a mixture is the percentage of isooctane in it. Gasolines burned in standard test engines are assigned octane numbers based on the compression ratio at which they begin to knock. A 90-octane fuel produces the same amount of knock as the 90% isooctane/10% heptane mixture. Branched-chain compounds produce less knock than straight-chain compounds. The octane numbers of two isomeric hexanes are



Petroleum Fractions

Fraction*	Principal Composition	Distillation Range (°C)
natural gas	$C_1 - C_4$	below 20
bottled gas	$C_5 - C_6$	20–60
gasoline	$C_4 - C_{12}$	40–200
kerosene	$C_{10} - C_{16}$	175–275
fuel oil, diesel oil	$C_{15} - C_{20}$	250–400
lubricating oils	$C_{18} - C_{22}$	above 300
paraffin	$C_{23} - C_{29}$	mp 50–60
asphalt	—	viscous liquid (“bottoms fraction”)
coke	—	solid

*Other descriptions and distillation ranges have been used, but all are similar.

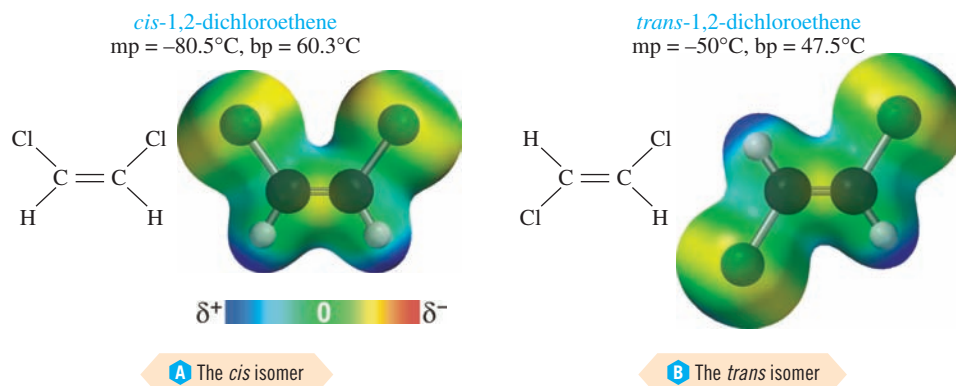


Figure 23-9 Two isomers of 1,2-dichloroethene are possible because rotation about the double bond is restricted. This is an example of *geometric* isomerism. An electrostatic charge potential plot is shown for each isomer.

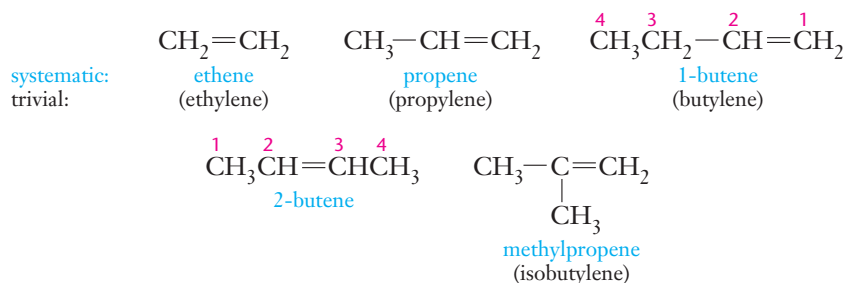
The root for the name of each alkene is derived from the alkane having the same number of C atoms as the longest chain containing the double bond. In the trivial (common) system of nomenclature, the suffix *-ylene* is added to the characteristic root. In systematic (IUPAC) nomenclature, the suffix *-ene* is added to the characteristic root.

SUMMARY OF IUPAC RULES FOR NAMING ALKENES AND CYCLOALKENES

1. Locate the C atoms in the *longest C chain that contains both carbons of the double bond*. Use the base name prefix with the ending *-ene*.
2. Number the C atoms of this chain sequentially *beginning at the end nearer the double bond*. Insert the number describing the position of the double bond (indicated by its *first* carbon location) before the base name. (This is necessary only for chains of four or more C atoms, because only one position is possible for a double bond in a chain of two or three carbon atoms.)
3. In naming alkenes, the double bond takes positional precedence over substituents on the carbon chain. The double bond is assigned the lowest possible number.
4. To name compounds with possible geometric isomers, consider the two largest groups within the carbon chain that contains the double bond—these are indicated as part of the base name. The isomer in which the largest groups at each end of the C=C are located on opposite sides is called *trans*. If the largest groups are on the same side, the molecule is referred to as *cis*. Insert the prefix *cis*- or *trans*- just before the number of the double bond to indicate whether the largest groups are on the same or opposite sides, respectively, of the double bond.
5. For cycloalkenes, the double bond is defined to be between C atoms 1 and 2, so no position number is needed to describe it.

► The prefix *trans*- means “across” or “on the other side of.” Words such as “transatlantic” will remind you of this terminology.

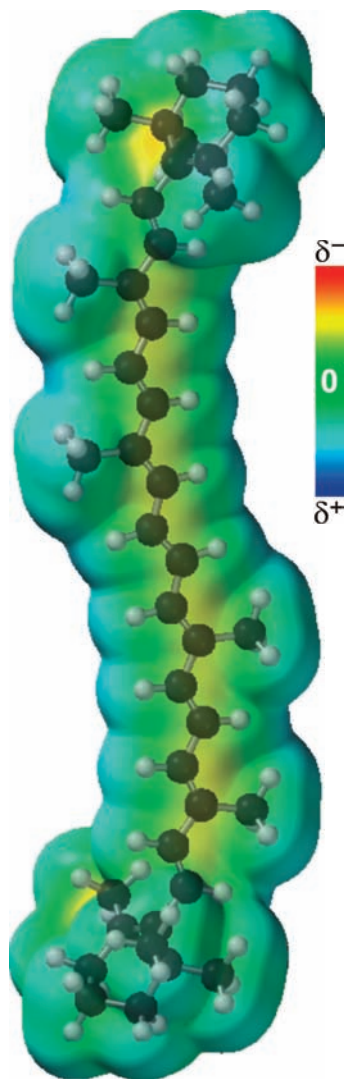
Some illustrations of this naming system follow.



► There are two isomers of 2-butene; they are *cis*-2-butene and *trans*-2-butene.

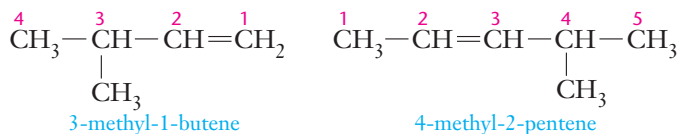


Charles D. Winters

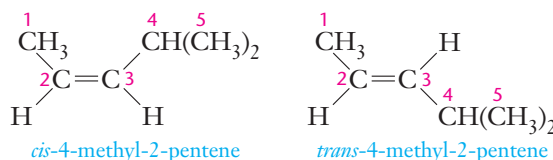


Carotene, the compound responsible for the orange-yellow color of these materials, contains 11 C=C bonds per molecule.

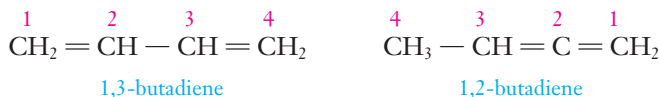
The following two names illustrate the application of Rule 3.



4-Methyl-2-pentene can exist as either of two geometric isomers. Their names illustrate the application of Rule 4.



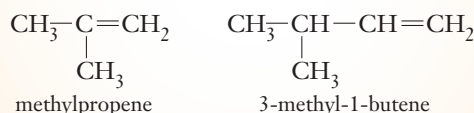
Some alkenes, called **polyenes**, have two or more carbon-carbon double bonds per molecule. The suffixes *-adiene*, *-atriene*, and so on are used to indicate the number of (C=C) double bonds in a molecule.



1,3-Butadiene and similar molecules that contain *alternating* single and double bonds are described as having **conjugated double bonds**. Such compounds are of special interest because of their polymerization reactions (see Section 23-19).

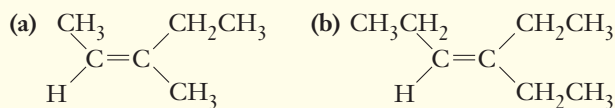
Problem-Solving Tip When Is the Location of a Substituent or a Multiple Bond Not Included in an IUPAC Name?

If only one location is possible for a substituent or double bond, the number that indicates the location can be left out of the compound's name. If there is doubt, put the number in the name. For example, "2-methyl-1-propene" is named simply methylpropene. There are no other possible locations for the substituent or the double bond. The name without the numbers is the correct name. Both numbers are necessary to name 3-methyl-1-butene, however.



EXAMPLE 23-6 Naming Alkenes

Give the IUPAC names of the following two alkenes.

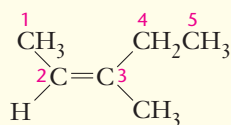


Plan

For each compound, we first find the longest chain that includes the double bond, and then number its C atoms beginning at the end nearer the double bond (Rules 1 and 2). Then we specify the identities and positions of substituents in the same way we did for alkanes. In (a) we specify the geometric isomer by locating the largest group attached to each of the double-bonded carbons and then describing their relationship using the *cis-trans* terminology.

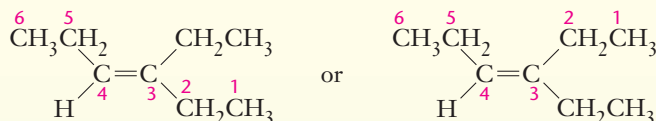
Solution

(a)



The longest such chain contains five atoms and has a double bond beginning at atom 2; thus, the compound is named as a derivative of 2-pentene. Now we must apply Rule 4. The two largest groups in the chain are the terminal —CH_3 (carbon 1) and the $\text{—CH}_2\text{CH}_3$ (carbons 4 and 5); these are on the *same side* of the double bond, so we name the compound as a derivative of *cis*-2-pentene. The only substituent is the methyl group at carbon 3. The full name of the compound is *cis*-3-methyl-2-pentene.

(b) There are two choices for the longest chain, and either one would have an ethyl substituent.

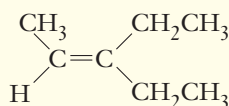


We could number either chain from the other end and still have the double bond starting at carbon 3; we number from the end that gives the carbon bearing the ethyl group the lowest possible position number, 3. Carbon 3 has two equivalent substituents, so geometric isomerism is not possible, and we do not use the *cis-trans* terminology. The name is 3-ethyl-3-hexene.

You should now work Exercise 20.

EXAMPLE 23-7 Naming Alkenes

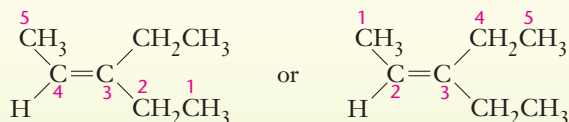
Name the following alkene.

**Plan**

As we did in Example 23-6(b), we first find the longest chain that includes the double bond, and then number it beginning at the end nearer the double bond (Rules 1 and 2). Then we specify the identities and positions of substituents in the same way we did for alkanes.

Solution

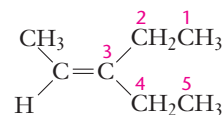
There are two choices for the longest chain, and either one would have an ethyl substituent.



Carbon 3 has two equivalent substituents, so geometric isomerism is not possible, and we do not use the *cis-trans* terminology. The name is 3-ethyl-2-pentene.

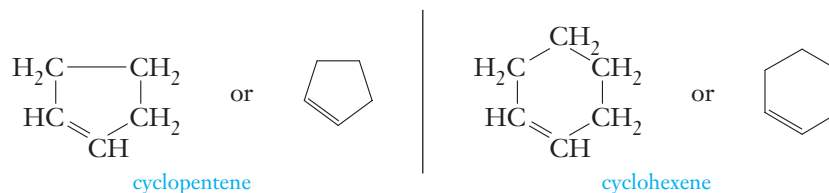
You should now work Exercise 22.

► One would not number the carbons as:



Rule 1 requires that we use the longest chain that includes both carbons of the double bond.

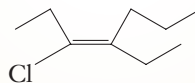
The cycloalkenes are represented by the general formula C_nH_{2n-2} . Two cycloalkenes and their skeletal representations are



Problem-Solving Tip How to Draw Skeletal Representations

The rules for drawing skeletal representations follow.

1. A carbon atom is assumed to be at each intersection of lines and at the end of each line. All carbon-carbon bonds are shown as lines. A carbon atom might be shown for clarity.
2. Because carbon has four bonds, we mentally supply hydrogens to give each carbon its four bonds.
3. Atoms other than hydrogen and carbon are shown. The following skeletal representation is that of *trans*-3-chloro-4-ethyl-3-heptene



and its formula is $C_9H_{17}Cl$.

EXAMPLE 23-8 Cycloalkenes

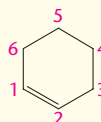
Write the skeletal representation of 3-methylcyclohexene.

Plan

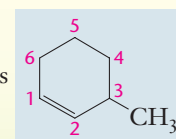
We draw the ring of the specified size with one double bond in the ring. We number the ring so that the double bond is between atoms 1 and 2. Then we add the designated substituents at the indicated positions.

Solution

We number the six-membered ring so that the double bond is between atoms 1 and 2.



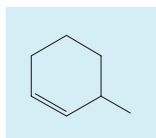
A methyl group is attached at carbon 3; the correct structure is



Remember that each intersection of two lines or the end of a line represents a carbon atom; there are enough H atoms at each C atom to make a total of four bonds to each carbon.

You should now work Exercise 21.

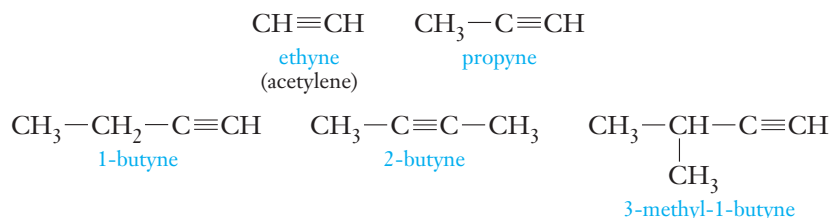
► The structure can also be written as



23-4 Alkynes

The **alkynes**, or acetylenic hydrocarbons, contain one or more carbon–carbon triple bonds, $\text{—C}\equiv\text{C—}$. The acyclic alkynes with one triple bond per molecule have the general formula $\text{C}_n\text{H}_{2n-2}$. The bonding in all alkynes is similar to that in acetylene (see Section 8-15). Triply bonded carbon atoms are sp -hybridized. The triply bonded atoms and their adjacent atoms lie on a straight line (Figure 23-10).

Alkynes are named like the alkenes except that the suffix *-yne* is added to the characteristic root. The first member of the series is commonly called acetylene. Its molecular formula is C_2H_2 . It is thermodynamically unstable, decomposing explosively to C(s) and $\text{H}_2\text{(g)}$ at high pressures. It may be converted into ethene (also known as ethylene) and then to ethane by the addition of hydrogen. The condensed formulas for several small alkynes are



The triple bond takes positional precedence over substituents on the carbon chain. It is assigned the lowest possible number in naming.

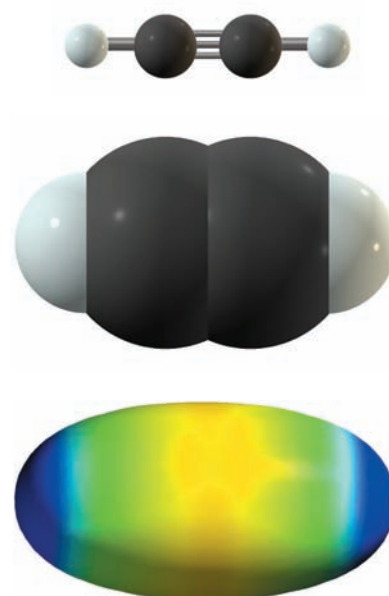


Figure 23-10 Models of acetylene, $\text{H—C}\equiv\text{C—H}$.

SUMMARY OF IUPAC RULES FOR NAMING ALKYNES

Alkynes are named like the alkenes except for the following two points.

1. The suffix *-yne* is added to the characteristic root.
2. The linear arrangement about the triple bond does not lead to geometric isomerism, so the prefixes *cis*- and *trans*- are not used.

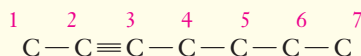
EXAMPLE 23-9 Alkynes

Write the structural formula of 5,5-dimethyl-2-heptyne.

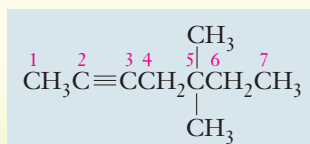
Plan

The structure is based on a seven-carbon chain with a triple bond beginning at carbon 2. We add methyl groups at the positions indicated.

Solution



Two methyl groups are attached to carbon 5, and sufficient hydrogens are added to complete the bonding at each C atom.



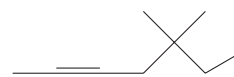
The carbon chain is numbered to give the triple bond the lowest possible numbers, even though that results in higher position numbers for the methyl substituents.

You should now work Exercise 28.



An oxy-acetylene torch uses acetylene as a fuel.

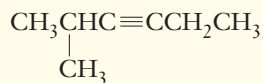
► The skeletal representation of 5,5-dimethyl-2-heptyne is



Unless otherwise noted, all content on this page is © Cengage Learning.

EXAMPLE 23-10 Naming Alkynes

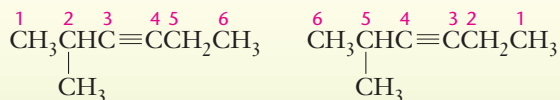
Give the IUPAC name of the compound

**Plan**

We find the longest chain and number it to give the triple bond the lowest possible number. Then we specify the substituent(s) by name and position number.

Solution

The longest continuous carbon chain that includes the triple bond has six C atoms. There are two ways in which we could choose and number such a chain, and in both the triple bond would be between C atoms 3 and 4.



Because we also want the methyl substituent to have the lowest possible number, we choose the first possibility. The name of the compound is **2-methyl-3-hexyne**.

You should now work Exercise 30.

Aromatic Hydrocarbons

Originally the word “aromatic” was applied to pleasant-smelling substances. The word now describes benzene, its derivatives, and certain other compounds that exhibit similar chemical properties. Some have very foul odors because of substituents on the benzene ring. On the other hand, many fragrant compounds do not contain benzene rings.

Steel production at one time required large amounts of coke. This was prepared by heating bituminous coal to high temperatures in the absence of air. This process also favors production of *coal gas* and *coal tar*. Because of the enormous amount of coal converted to coke, coal tar was produced in large quantities. It served as a source of aromatic compounds. For each ton of coal converted to coke, about 5 kg of aromatic compounds were obtained. Today petroleum refining is the major source of aromatic hydrocarbons.

Early research on the reactions of the aromatic hydrocarbons led to methods for preparing a great variety of dyes, drugs, flavors, perfumes, and explosives. More recently, large numbers of polymeric materials, such as plastics and fabrics, have been prepared from these compounds.

► The main components of coal gas are hydrogen (≈50%) and methane (≈30%).

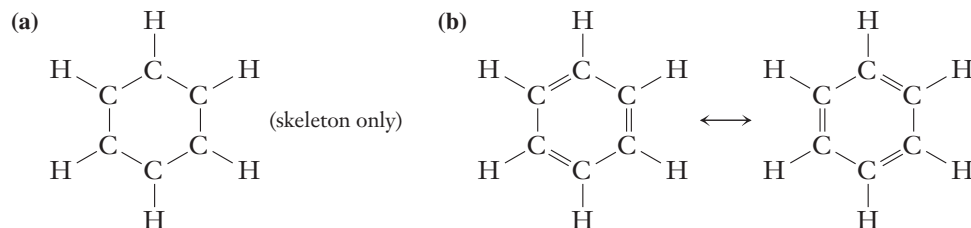
► Distillation of coal tar produces a variety of aromatic compounds.

23-5 Benzene

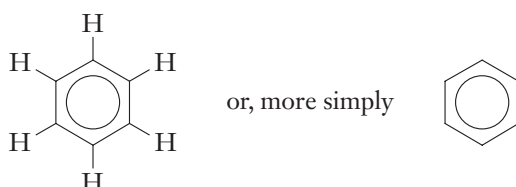
Benzene is the simplest aromatic hydrocarbon. By studying its reactions, we can learn a great deal about aromatic hydrocarbons. Benzene was discovered in 1825 by Michael Faraday when he fractionally distilled a by-product oil obtained in the manufacture of illuminating gas from whale oil.

Elemental analysis and determination of its molecular weight show that the molecular formula for benzene is C_6H_6 . The formula suggests that it is highly unsaturated. But its properties are quite different from those of alkenes and alkynes.

The facts that only one monosubstitution product is obtained in many reactions and that no additional products can be prepared show conclusively that benzene has a *symmetrical ring structure*. Stated differently, every H atom is equivalent to every other H atom, and this is possible only in a symmetrical ring structure (a).



The debate over the structure and bonding in benzene raged for at least 30 years. In 1865, Friedrich Kekulé (1829–1896) suggested that the structure of benzene was intermediate between two structures [part (b) of the structures shown above] that we now call resonance structures. We often represent benzene as



All 12 atoms in a benzene molecule lie in a plane. This suggests sp^2 hybridization of each carbon. The six sp^2 -hybridized C atoms lie in a plane, and the unhybridized p orbitals extend above and below the plane. Side-by-side overlap of the p orbitals forms pi orbitals (see Figure 9-11). The electrons associated with the pi bonds are *delocalized* over the entire benzene ring (Figure 23-11a, b).

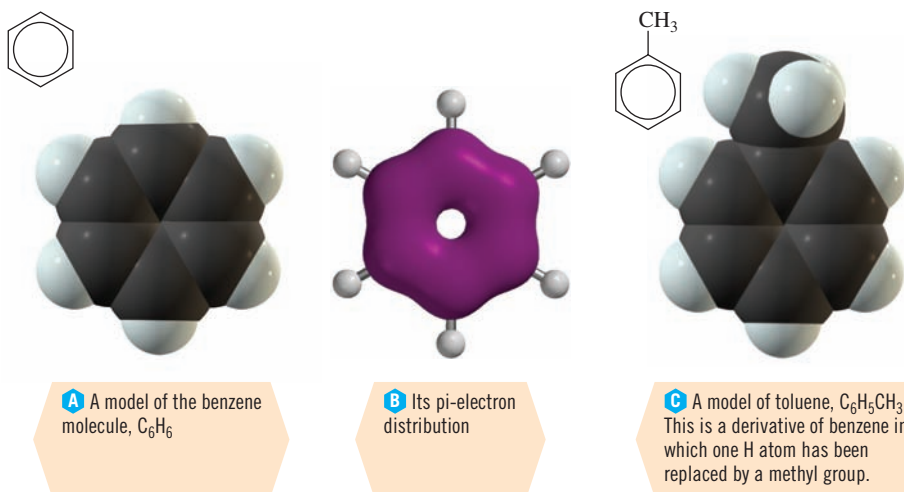
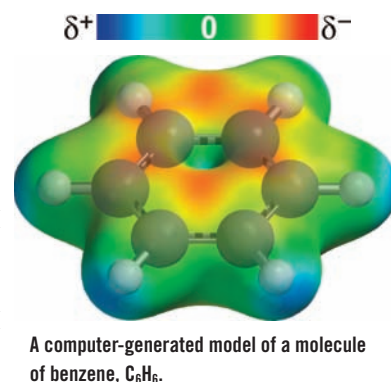


Figure 23-11



► The structure of benzene is described in detail in terms of MO theory in Section 9-6.



Each of these products contains compounds based on the benzene ring.

23-6 Other Aromatic Hydrocarbons

Benzene molecules bearing alkyl substituents are called **alkylbenzenes**. The simplest of these is methylbenzene (common name, toluene), shown in Figure 23-11c. The dimethyl benzenes are called xylenes. Three different compounds (Table 23-6) have the formula $C_6H_4(CH_3)_2$ (see margin). These three xylenes are *constitutional isomers*. In naming these (as well as other disubstituted benzenes), we use the prefixes *ortho-* (abbreviated *o-*), *meta-* (*m-*), or *para-* (*p-*) to refer to relative positions of substituents on the benzene ring. The

Unless otherwise noted, all content on this page is © Cengage Learning.

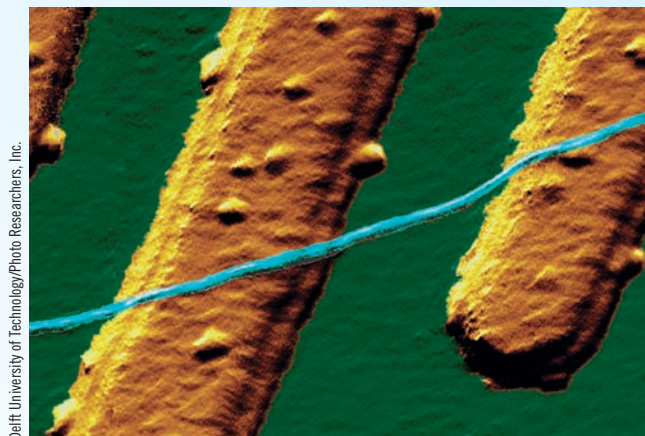
Nanotechnology

Chemists are very adept at thinking about matter at the atomic and molecular level. But to control the physical characteristics of everyday materials, we must first relate *molecular* properties to *bulk* properties. For example, an individual molecule's shape and dipole moment influence the strength of interactions *between* molecules, which in turn determine the melting point of a solid made up of *many* of these molecules. A clear understanding of such microscopic/macroscopic chemical relationships is what allows scientists and engineers to create materials suitable for specific uses. But what if we could “engineer” directly at the molecular level? An emerging discipline known as *nanotechnology* concerns precisely that: designing molecule-sized devices to do the work of objects we've traditionally manipulated on a much larger scale.

Since a chemical bond is on the order of 1–5 Å in length (1 angstrom = 1×10^{-10} meter), molecules and small assemblages of molecules have sizes of up to a few hundred nanometers (1 nanometer = 1×10^{-9} meter). At this level, chemical particles have not yet reached the critical mass necessary for bulk behavior and still behave like individual molecules in some ways. As a result, these “nanoparticles” often possess unusual or superior properties compared to larger structures.

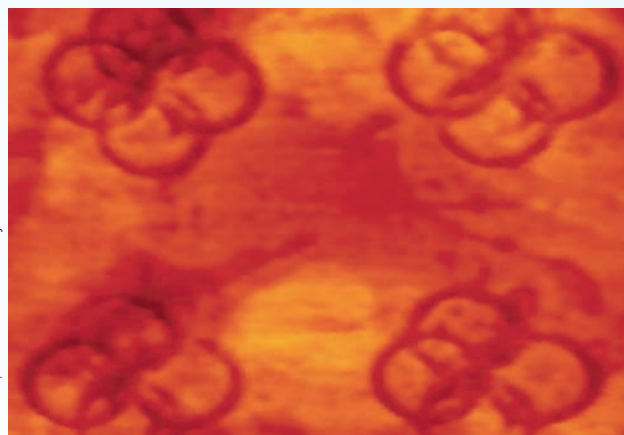
One highly anticipated application of nanotechnology is molecular electronics, in which computer chip components (now reaching the lower size limits achievable with regular fabrication techniques) may be replaced with faster, more space-efficient devices made from individual molecules. For example, carbon nanotubes, tiny hollow structures composed entirely of carbon atoms, could potentially be used in this manner because their excellent thermal and electrical conductivity allows them to function as molecular “wires.” While regular wires drawn from conducting metals always contain some property-limiting defects, the single-molecule nature of carbon nanotubes renders them free of imperfections. Their flawless structures also generate other unique properties, such as a strength per unit weight much greater than that of steel. Carbon nanotubes have already been used to toughen lightweight, high-end sports equipment such as golf clubs and bicycle frames.

Because many biological structures are nanoscale in size, the treatment of cancer and other diseases may derive immense benefits from nanotechnology. Particles smaller than approximately 50 nm in diameter can enter most cells, while those smaller than 20 nm can pass through the walls of blood vessels to surrounding tissues, allowing these materials to go easily where they are needed. Additionally, the molecular nature of nanomaterials means they can be precisely modified by chemical attachment of various substances required for diagnosis and therapy. A single anticancer nanoparticle, constructed from a large polymer or protein molecule, might simultaneously bear an antibody that selectively binds to cancerous cells (increasing the efficacy of treatment), a magnetic contrast agent for MRI imaging, and the actual drug molecules used for therapy. These tiny, multifunctional super-medications of the future are called “nanoclinics.”



Delft University of Technology/Photo Researchers, Inc.

A colored atomic force microscope (AFM) image of a carbon nanotube wire (blue) on platinum electrodes (yellow). The nanotube is 1.5 nm across, a mere 10 atoms wide. This is considered to be the world's smallest electrical wire. Besides the potential to miniaturize electronic components, the nanotube's small size gives it special properties that could be used to make entirely new electronic devices.



Jane Carno, Louisiana State University

Image of 100-nm-wide circular patterns etched by the nanometer-wide tip of an atomic force microscope probe onto a gold surface covered by long-chain organic molecules. Darker colors indicate lower regions on the surface. The circle grooves are about 10 nm wide and 1 nm deep. The ability to design and create scale objects on surfaces is an important part of nanotechnology.

Curing cancer and reinventing the computer chip seem sufficiently ambitious for any new technology. But nanotechnology has captured our imaginations to such an extent that a number of other, more wild-eyed proposals for its use have also appeared. These include artificial intestines made from nanoparticle-laden plastic films, “smart” bullets with tiny target-tracking computer chips, and a “space elevator” consisting of a 22,000-mile carbon nanotube-fiber rope connecting the Earth to a satellite, used to hoist materials into orbit without the use of rockets. Whether or not these rather fantastic technologies ever come to pass, one thing appears certain given nanotechnology's more pragmatic uses: Many of the “big things” in our future may actually be very small.

LISA SAUNDERS BAUGH

Table 23-6 Aromatic Hydrocarbons from Coal Tar

Name	Formula	Normal bp (°C)	Normal mp (°C)	Solubility
benzene	C ₆ H ₆	80	+6	All insoluble in water
toluene	C ₆ H ₅ CH ₃	111	−95	
<i>o</i> -xylene	C ₆ H ₄ (CH ₃) ₂	144	−27	
<i>m</i> -xylene	C ₆ H ₄ (CH ₃) ₂	139	−48	
<i>p</i> -xylene	C ₆ H ₄ (CH ₃) ₂	138	+13	
naphthalene	C ₁₀ H ₈	218	+80	
anthracene	C ₁₄ H ₁₀	342	+218	
phenanthrene	C ₁₄ H ₁₀	340	+101	

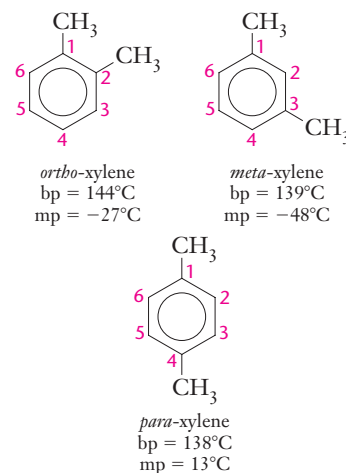
ortho- prefix refers to two substituents located on *adjacent* carbon atoms; for example, 1,2-dimethylbenzene is *o*-xylene. The *meta*- prefix identifies substituents on C atoms 1 and 3, so 1,3-dimethylbenzene is *m*-xylene. The *para*- prefix refers to substituents on C atoms 1 and 4, so 1,4-dimethylbenzene is *p*-xylene.

SUMMARY OF RULES FOR NAMING DERIVATIVES OF BENZENE

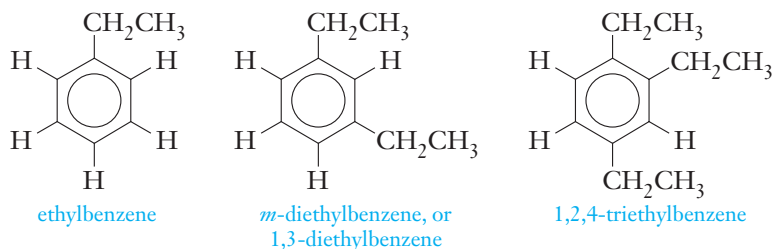
1. If there is only one group on the ring, no number is needed to designate its position.
2. If there are two groups on the ring, we use the traditional designations.

ortho- or *o*- for 1,2-disubstitution
meta- or *m*- for 1,3-disubstitution
para- or *p*- for 1,4-disubstitution

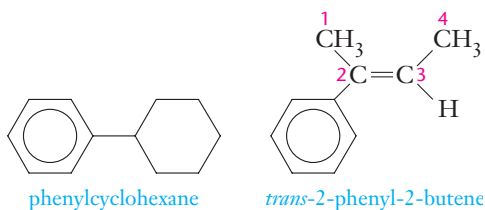
3. If there are three or more groups on the ring, location numbers are assigned to give the minimum sum of numbers.



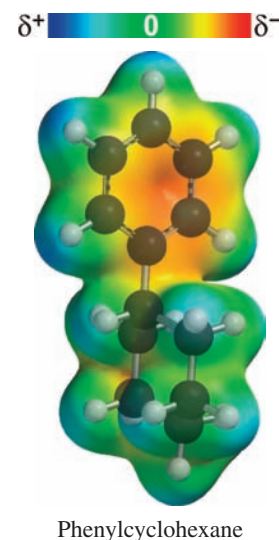
Examples are



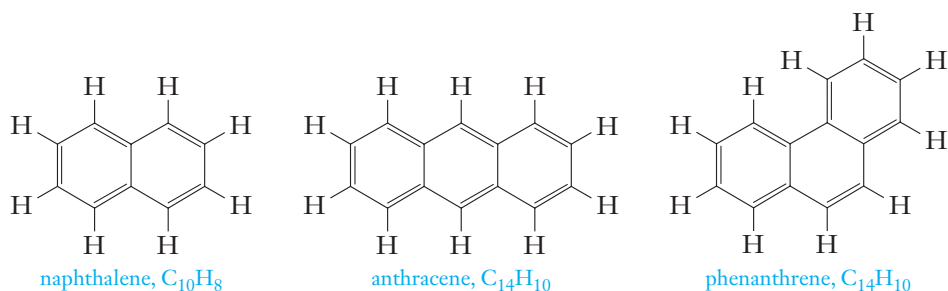
When an H atom is removed from a benzene molecule, C₆H₆, the resulting group, C₆H₅ — or , is called “phenyl.” Sometimes we name mixed alkyl-aromatic hydrocarbons on that basis.



Another class of aromatic hydrocarbons consists of “condensed” or “fused-ring” aromatic systems. The simplest of these are naphthalene, anthracene, and phenanthrene.

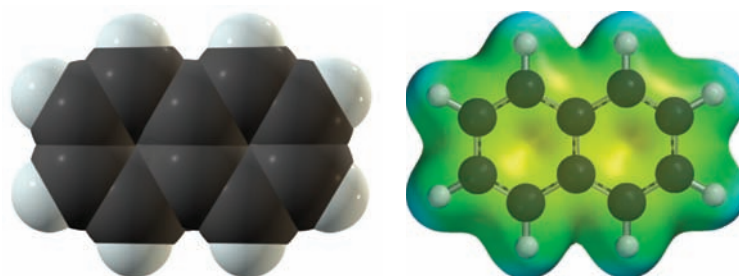


Unless otherwise noted, all content on this page is © Cengage Learning.



No hydrogen atoms are attached to the carbon atoms that are involved in fusion of aromatic rings, that is, carbon atoms that are members of two or more aromatic rings.

The traditional name is often used as part of the base name in naming an aromatic hydrocarbon and its derivatives. You should know the names and structures of the aromatic hydrocarbons discussed thus far: benzene, toluene, the three xylenes, naphthalene, anthracene, and phenanthrene.



Naphthalene

Distillation of coal tar provides four volatile fractions, as well as the pitch that is used for surfacing roads and in the manufacture of “asphalt” roofing (Figure 23-12). Eight aromatic hydrocarbons obtained in significant amounts by efficient fractional distillation of the “light oil” fraction are listed in Table 23-6.

23-7 Hydrocarbons: A Summary

Hydrocarbons contain only carbon and hydrogen. They can be subdivided into various groups. To assist you in organizing what you have studied so far in this chapter, take a few minutes and study Figure 23-13.

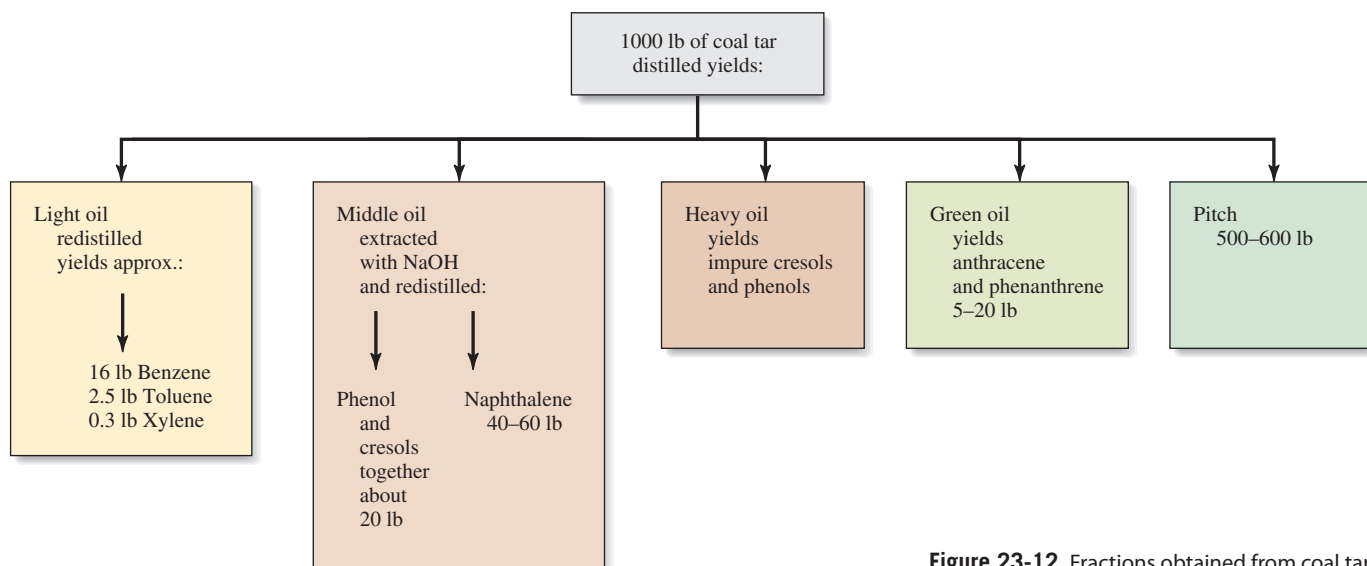
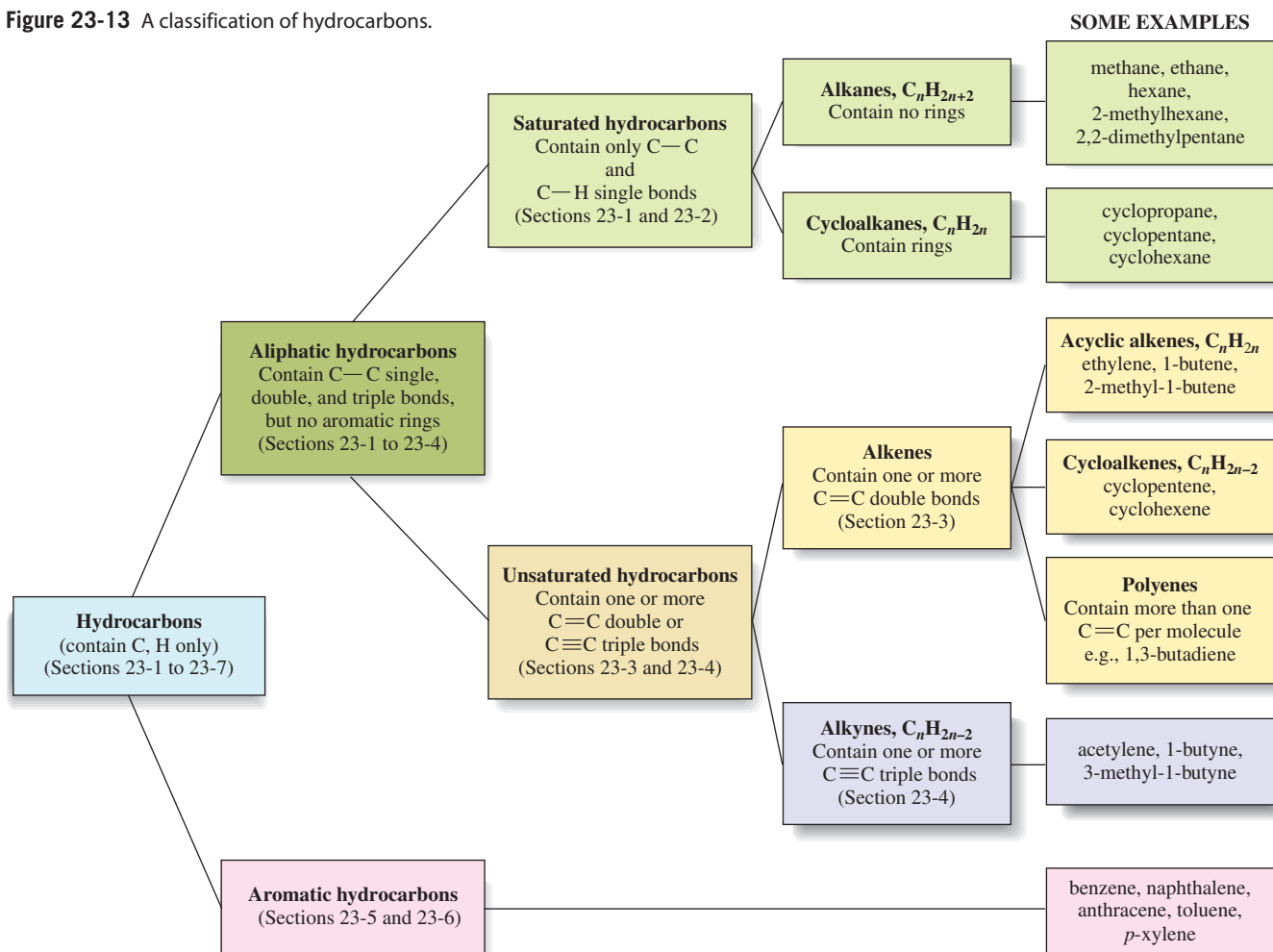


Figure 23-12 Fractions obtained from coal tar.

Figure 23-13 A classification of hydrocarbons.

Functional Groups

The study of organic chemistry is greatly simplified by considering hydrocarbons as parent compounds and describing other compounds as derived from them. In general, an organic molecule consists of a skeleton of carbon atoms with special groups of atoms attached to that skeleton. These special groups of atoms are often called **functional groups** because they represent the most common sites of chemical reactivity (function). The only functional groups that are possible in hydrocarbons are double and triple (i.e., pi) bonds. Atoms other than C and H are called **heteroatoms**, the most common being O, N, S, P, and the halogens. Most functional groups contain one or more heteroatoms.

In the next several sections, we will introduce some common functional groups that contain heteroatoms and learn a little about the resulting classes of compounds. We will continue to represent alkyl groups with the symbol $R-$. We commonly use that symbol to represent either an aliphatic (e.g., alkyl) or an aromatic (e.g., an aryl, such as phenyl) group. When we specifically mean an aryl group, we will use the symbol $Ar-$.

► As you study the following sections, you may wish to refer to the summary in Section 23-15.

► An **alkyl group** is a group of atoms derived from an alkane by the removal of one hydrogen atom. An **aryl group** is a group of atoms derived from an aromatic system by the removal of one hydrogen atom. The simplest aryl group is phenyl, $-C_6H_5$, derived from benzene, C_6H_6 .

23-8 Organic Halides

Almost any hydrogen atom in a hydrocarbon can be replaced by a halogen atom to give a stable compound. Table 23-7 shows some organic halides and their names.

In the IUPAC naming system, the organic halides are named as *halo-* derivatives of the parent hydrocarbons. The prefix *halo-* can be *fluoro-*, *chloro-*, *bromo-*, or *iodo-*. Simple alkyl

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 23-7 Some Organic Halides

Formula	Structural Formula	Ball-and-Stick Model	Electrostatic Charge Potential Plot	bp (°C)	IUPAC Name Common Name
CH ₃ Cl				-23.8	chloromethane methyl chloride
CH ₂ Cl ₂				40.2	dichloromethane methylene chloride
CHCl ₃				61	trichloromethane chloroform
CCl ₄				76.8	tetrachloromethane carbon tetrachloride
CHCl ₂ Br				90	bromodichloromethane
(CH ₃) ₂ CHI				89.5	2-iodopropane isopropyl iodide
C ₅ H ₇ Cl				25	3-chlorocyclopentene (other isomers possible)
C ₆ H ₅ I				118	iodobenzene phenyl iodide
C ₆ H ₄ ClBr				204	1-bromo-2-chloro- benzene (other isomers possible) <i>o</i> -bromochlorobenzene
C ₁₄ H ₉ Cl ₅					1,1,1-trichloro-2, 2-bis(<i>p</i> -chlorophenyl)- ethane DDT

chlorides are sometimes given common names as alkyl derivatives of the hydrogen halides. For instance, the IUPAC name for $\text{CH}_3\text{CH}_2\text{—Cl}$ is chloroethane; it is commonly called ethyl chloride by analogy to H—Cl , hydrogen chloride.

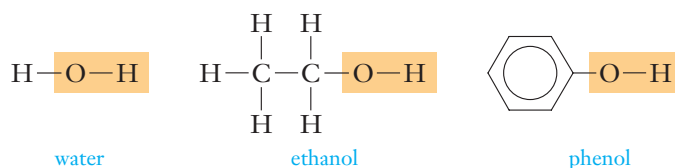
A carbon atom can be bonded to as many as four halogen atoms, so an enormous number of organic halides can exist. Completely fluorinated compounds are known as *fluorocarbons* or sometimes *perfluorocarbons*. The fluorocarbons are even less reactive than hydrocarbons. Saturated compounds in which all H atoms have been replaced by some combination of Cl and F atoms are called *chlorofluorocarbons* or sometimes *freons*. These compounds were widely used as refrigerants and as propellants in aerosol cans. However, the release of chlorofluorocarbons into the atmosphere has been shown to be quite damaging to the earth's ozone layer. Since January 1978, the use of chlorofluorocarbons in aerosol cans in the United States has been prohibited, and efforts to develop both controls for existing chlorofluorocarbons and suitable replacements continue. The production and sale of freons have been banned in many countries.

► Freon is a DuPont trademark for certain chlorofluorocarbons; other companies' related products are known by other names. Typical freons are trichlorofluoromethane, CFCl_3 (called Freon-11), and dichlorodifluoromethane, CF_2Cl_2 (called Freon-12).

23-9 Alcohols and Phenols

Alcohols and phenols contain the hydroxyl group (—O—H) as their functional group. **Alcohols** may be considered to be derived from saturated or unsaturated hydrocarbons by the replacement of at least one H atom by a hydroxyl group. The properties of alcohols result from a hydroxyl group attached to an *aliphatic* carbon atom, —C—O—H . Ethanol (ethyl alcohol) is the most common example (Figure 23-14).

When a hydrogen atom on an aromatic ring is replaced by a hydroxyl group (Figure 23-15), the resulting compound is known as a **phenol**. Such compounds behave more like acids than alcohols. Alternatively, we may view alcohols and phenols as derivatives of water in which one H atom has been replaced by an organic group.



► The simplest phenol is called phenol. The most common member of a class of compounds is often called by the class name. Salt, sugar, alcohol, and phenol are examples.

Indeed, this is a better view. The structure of water was discussed in Section 8-9. The hydroxyl group in an alcohol or a phenol is covalently bonded to a carbon atom, but the

► In Example 18-14 we compared the acid strengths of phenol, water, and ethanol.



Figure 23-14 Models of ethanol (also called ethyl alcohol or grain alcohol), $\text{CH}_3\text{CH}_2\text{OH}$.

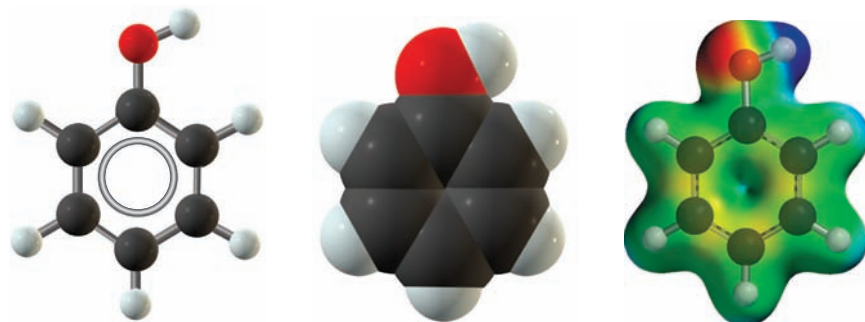


Figure 23-15 Models of phenol, $\text{C}_6\text{H}_5\text{OH}$.

 CHEMISTRY IN USE

Developing More Environmentally Friendly Solvents

Today's chemists are increasingly concerned about the environmental impacts of solvents and solutions. Each year, billions of gallons of water and organic solvents are used for chemical manufacturing, textile dyeing, industrial cleaning, and food processing. These materials must undergo costly, energy-intensive decontamination procedures before they can be reused. Even worse, the accidental release of organic solvents and incompletely treated water into the environment leads to groundwater pollution and the buildup of greenhouse gases. Scientists and engineers are actively seeking new technologies to help reduce and replace the vast quantities of commercial solvents currently in use.

Dry cleaning is an example of an industry undergoing adaptation to more benign solvent technologies. While most dry cleaning operations utilize highly toxic perchloroethylene as a cleaning solvent, some stores are now using what might appear to be an unlikely replacement: carbon dioxide. CO_2 can be liquefied at ambient temperatures by pressurization to above 650 psig (44.2 atm). Carbon dioxide-based dry cleaning involves treating clothes with specially formulated detergents in a washer pressurized with CO_2 at 700 psig (47.6 atm). Unlike perchloroethylene-based processes that require heating, CO_2 cleaning is carried out at room temperature, minimizing wear and tear on garments and reducing energy costs. When the cleaning cycle is complete and most of the dirt-bearing liquid CO_2 has been drained away, the clothes are “dried” by simply returning the washer to ambient pressure to remove residual carbon dioxide as a gas. More than 98% of the CO_2 used in each cleaning cycle is recovered for reuse. This process is currently in use by the Hangers chain of cleaners in North America and Europe.

Another promising technology is fluorous-phase extraction, which functions by expanding on the principles “like dissolves like” and “oil and water don't mix.” The immiscibility of nonpolar organic solvents with water, in conjunction with the solubility preferences shown by most solutes for one of these two media, is commonly exploited in chemical syntheses to separate reaction products from unwanted byproducts and unused reagents. Fluorinated organic compounds such as perfluorohexane ($\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$) are often immiscible with both organic solvents and water, and will actually form a *third* liquid layer (the fluorous phase) in the presence of aqueous and nonpolar solutions at ambient temperatures (see the accompanying figure). Solutes that contain large numbers of fluorine atoms in their structures can exhibit extremely selective preferences for the fluorous phase. This characteristic can be exploited to separate them efficiently from nonfluorinated materials.

A typical chemical synthesis utilizing fluorous-phase extraction might involve combining two immiscible solutions—the first a nonpolar organic solvent containing reagents, and the second a fluorinated solvent containing a catalyst that has been specially modified to have fluorous-phase solubility. Heating this mixture results in the temporary miscibility of the two solutions, allowing the reactants and catalyst to mix and the desired reaction to occur. When the mixture is subsequently cooled, the nonpolar organic and fluorous phases separate back into individual layers, leaving the reaction products in the nonpolar organic phase, and selectively trapping the catalyst (often an expensive or environmentally unfriendly material) in the fluorous phase where it can be efficiently recovered.

Solvents will always be a necessary part of industrial operations. While they can never be completely eliminated, researchers and regulators can work to accelerate the development and

O—H bond is quite polar. The oxygen atom has two unshared electron pairs, and the C—O—H bond angle is nearly 104.5° .

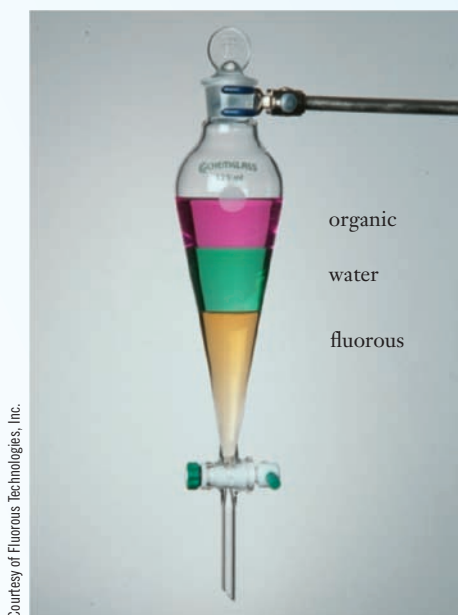
The presence of a bonded alkyl or aryl group changes the properties of the —OH group. *Alcohols* are so very weakly acidic that they are thought of as neutral compounds. *Phenols* are weakly acidic.

Many properties of alcohols depend on whether the hydroxyl group is attached to a carbon that is bonded to *one*, *two*, or *three* other carbon atoms.

Primary alcohols contain one R group; **secondary alcohols** contain two R groups; and **tertiary alcohols** contain three R groups bonded to the carbon atom to which the —OH group is attached.

implementation of “greener,” more ecologically beneficial technologies. When it comes to environmental concerns, chemists are working hard to ensure that solvents will one day no longer be part of the problem, but rather—both literally and metaphorically speaking—part of the solution!

LISA SAUNDERS BAUGH



Courtesy of Fluorous Technologies, Inc.

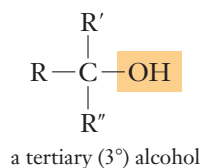
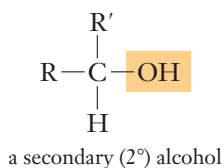
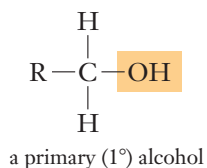
When mixed, a nonpolar organic solvent (*top*), water (*middle*), and a fluorinated solvent (*bottom*) separate into three distinct phases (here containing colored dyes).



By permission of Thomas Swan & Co Ltd UK

Supercritical CO_2 fluid extraction of caffeine from coffee beans is used by an increasing number of companies to produce “decaf” coffee. After the coffee beans are soaked in water to bring the caffeine closer to the surface, they are placed under approximately 35 atm of CO_2 at room temperature. This selectively extracts more than 98% of the caffeine from the beans with minimal effect on flavor and aroma. The caffeine is soluble in the supercritical CO_2 , but precipitates when the pressure is lowered to convert the supercritical fluid to gaseous CO_2 .

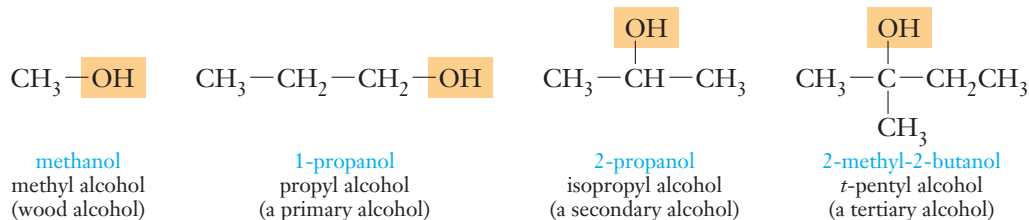
Representing alkyl groups as R, we can illustrate the three classes of alcohols. The R groups may be the same or different.



► In writing organic structures, we often use primes when we wish to specify that the alkyl groups might be different, for example, R, R', R''.

Nomenclature

The systematic name of an alcohol consists of the root name plus an *-ol* ending. A numeric prefix indicates the position of the —OH group on a chain of three or more carbon atoms.



► Acyclic compounds contain no rings.



Charles Steele

Polyols are used in permanent antifreeze and in cosmetics.

EXAMPLE 23-11 Formulas of Alcohols

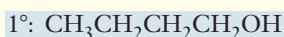
There are four constitutional isomers of the saturated acyclic four-carbon alcohols with one —OH per molecule. Write the structural formula of each, and identify each as primary, secondary, or tertiary. Name each isomer.

Plan

The carbon skeleton can be either a straight chain, C—C—C—C , or branched, $\begin{array}{c} \text{C—C—C} \\ | \\ \text{C} \end{array}$.

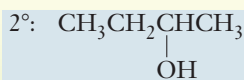
Each skeleton has two different types of carbons to which the —OH group can be attached.

Solution



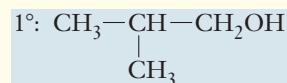
1-butanol

butyl alcohol



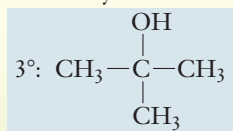
2-butanol

secondary butyl alcohol



2-methyl-1-propanol

isobutyl alcohol

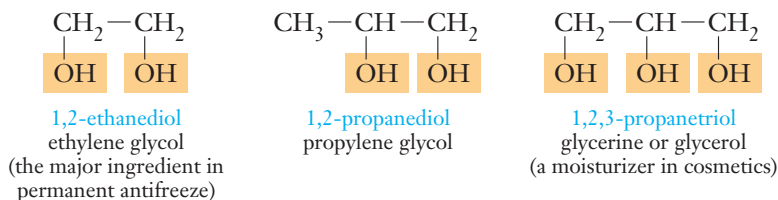


2-methyl-2-propanol

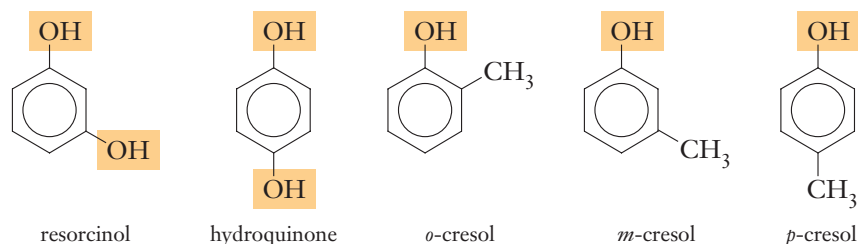
tertiary butyl alcohol

You should now work Exercise 46.

The **polyols** are alcohols that contain more than one —OH group per molecule. Those containing two —OH groups per molecule are called *glycols*. Important examples of polyols include



Phenols are usually referred to by their common names. Examples are

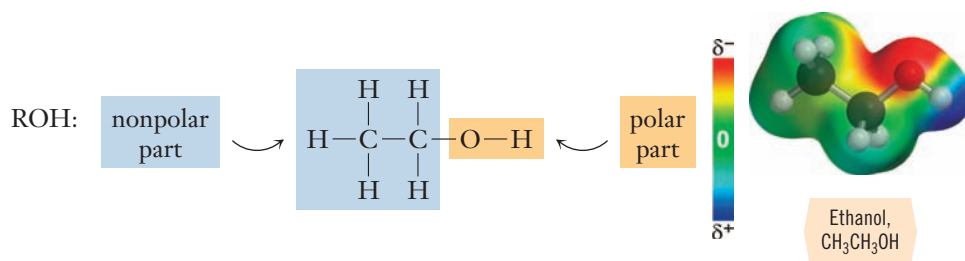


► The *o*-, *m*-, and *p*- notation was introduced in Section 23-6.

As you might guess, cresols occur in “creosote,” a wood preservative.

Physical Properties

The hydroxyl group, —OH , is quite polar, whereas alkyl groups, R , are nonpolar. The properties of alcohols depend on two factors: (1) the number of hydroxyl groups per molecule, and (2) the size of the nonpolar portion of the molecule.



The low-molecular-weight alcohols are soluble in water in all proportions (miscible). Beginning with the four butyl alcohols, solubility in water decreases rapidly with increasing molecular weight. This is because the nonpolar parts of such molecules are much larger than the polar parts. Many polyols are very soluble in water because they contain two or more polar —OH groups per molecule.

Table 23-8 shows that the boiling points of unbranched primary alcohols increase, and their solubilities in water decrease, with increasing molecular weight. The boiling points of alcohols are much higher than those of the corresponding alkanes (see Table 23-2) because of the hydrogen bonding of the hydroxyl groups.

Phenols are solids at 25°C . Phenols are only slightly soluble in water unless they contain other functional groups that interact with water.

Uses

Many alcohols and phenols have considerable commercial importance. Methanol, CH_3OH , was formerly produced by the destructive distillation of wood and is sometimes

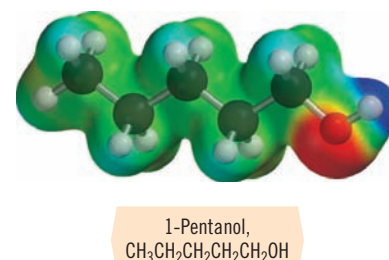
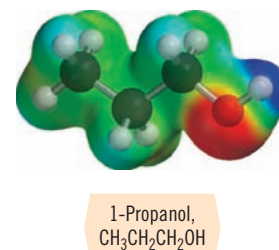
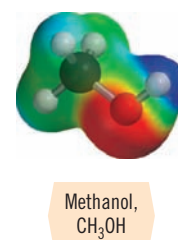


Table 23-8 Physical Properties of Primary Alcohols

Name	Formula	Normal bp ($^\circ\text{C}$)	Solubility in H_2O (g/100 g at 20°C)
methanol	CH_3OH	65	miscible
ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	78.5	miscible
1-propanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	97	miscible
1-butanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	117.7	7.9
1-pentanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	137.9	2.7
1-hexanol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	155.8	0.59

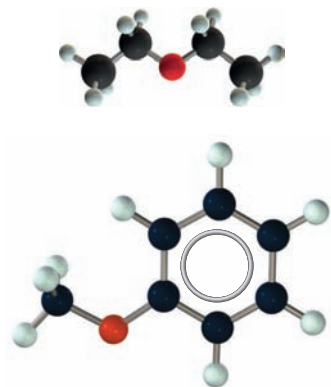
As the number of nonpolar CH_2 groups increases, the alcohol molecules become less polar, decreasing their solubility in water. The greenish areas on the electrostatic charge potential (ECP) surfaces represent nonpolar regions where the atomic charges are near zero. The boiling points also rise with the increasing molecular weights and increasing dispersion forces between the nonpolar regions of adjacent molecules.

► Fermentation is an enzymatic process carried out by certain kinds of yeast.

called wood alcohol. It is now produced in large quantities from carbon monoxide and hydrogen. It is very toxic and causes permanent blindness when taken internally.

Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, also known as ethyl alcohol or grain alcohol, can be prepared by fermentation of sugar. The most ancient written literature refers to beverages that were obviously alcoholic!

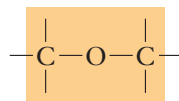
Many simple alcohols are important raw materials in the industrial synthesis of polymers, fibers, explosives, plastics, and pharmaceutical products. Phenols are widely used in the preparation of plastics and dyes. Solutions of phenols are used as antiseptics and disinfectants. Some uses of polyols depend on their relatively high boiling points. For instance, glycerine is used as a wetting agent in cosmetic preparations. Ethylene glycol (bp = 197°C), which is miscible with water, is used in commercial permanent antifreeze.



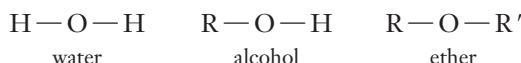
Models of diethyl ether (top) and methyl phenyl ether (bottom).

23-10 Ethers

When the word “ether” is mentioned, most people think of the well-known anesthetic, diethyl ether. There are many ethers. Their uses range from artificial flavorings to refrigerants and solvents. An **ether** is a compound in which an O atom is bonded to two organic groups.

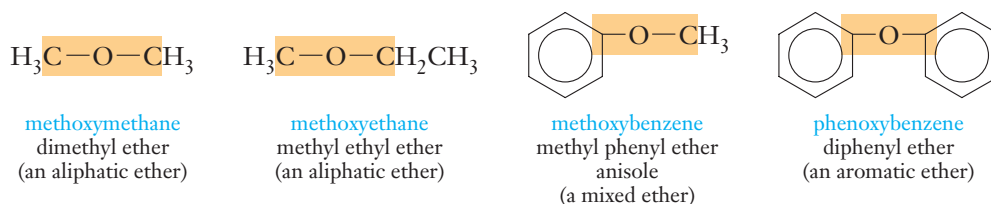


Alcohols are considered derivatives of water in which one H atom has been replaced by an organic group. Ethers may be considered derivatives of water in which both H atoms have been replaced by organic groups.



The similarity is only structural, however, because ethers are only slightly polar and are chemically rather unreactive. In fact, their physical properties are similar to those of the corresponding alkanes; for example, CH_3OCH_3 is like $\text{CH}_3\text{CH}_2\text{CH}_3$.

Three kinds of ethers are known: (1) aliphatic, (2) aromatic, and (3) mixed. Common names are used for ethers in most cases.



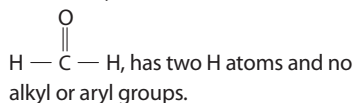
► When the benzene ring is a substituent, it is called a phenyl group (— C_6H_5).

Diethyl ether is a very low boiling liquid (bp = 35°C). Dimethyl ether is a gas that is used as a refrigerant. The aliphatic ethers of higher molecular weights are liquids, and the aromatic ethers are liquids and solids.

Even ethers of low molecular weight are only slightly soluble in water. Diethyl ether is an excellent solvent for organic compounds. It is widely used to extract organic compounds from plants and other natural sources.

23-11 Aldehydes and Ketones

► The simplest aldehyde, formaldehyde,



Aldehydes and ketones contain the carbonyl group, >C=O . In **aldehydes**, at least one H atom is bonded to the carbonyl group. **Ketones** have two carbon atoms bonded to a carbonyl group. Models of formaldehyde (the simplest aldehyde) and acetone (the simplest ketone) are shown in Figure 23-16.

Unless otherwise noted, all content on this page is © Cengage Learning.

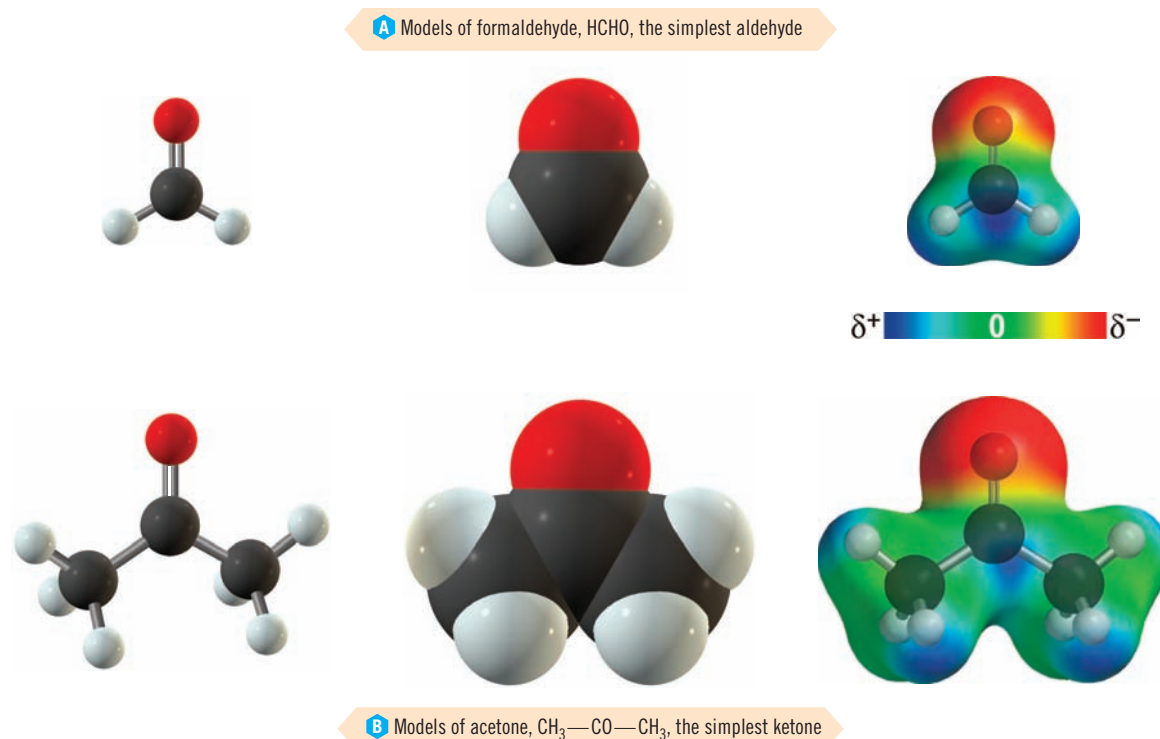
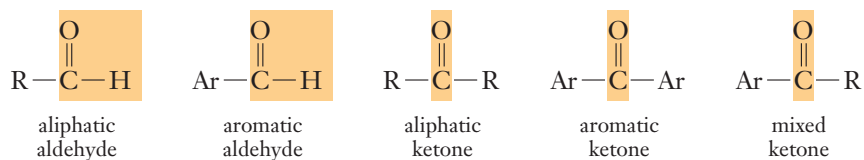
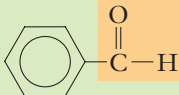


Figure 23-16 Models of the lowest molecular weight aldehyde and ketone.



Aldehydes are usually called by their common names. These are derived from the name of the acid with the same number of C atoms (Table 23-9). The systematic (IUPAC) name is derived from the name of the parent hydrocarbon. The suffix *-al* is added to the characteristic stem. The carbonyl group takes positional precedence over most other substituents.

Table 23-9 Properties of Some Simple Aldehydes

Common Name	Formula	Normal bp (°C)
formaldehyde (methanal)	$\text{H—}\overset{\text{O}}{\parallel}\text{C—H}$	−21
acetaldehyde (ethanal)	$\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—H}$	20.2
propionaldehyde (propanal)	$\text{CH}_3\text{CH}_2\text{—}\overset{\text{O}}{\parallel}\text{C—H}$	48.8
benzaldehyde		179.5

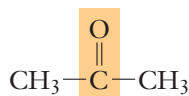


Charles D. Winters

Acetone is the active ingredient in some nail polish removers.

Formaldehyde has long been used as a disinfectant and as a preservative (including embalming fluid) for biological specimens. Its main use is in the production of certain plastics and in binders for plywood. Many important natural substances are aldehydes and ketones. Examples include sex hormones, some vitamins, camphor, and the flavorings extracted from almonds and cinnamon. Aldehydes contain a carbon–oxygen double bond, so they are very reactive compounds. As a result, they are valuable in organic synthesis, particularly in the construction of carbon chains.

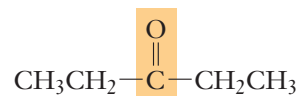
The simplest ketone is called acetone. Other simple, commonly encountered ketones are usually called by their common names. These are derived by naming the alkyl or aryl groups attached to the carbonyl group.



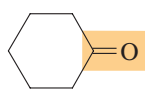
acetone



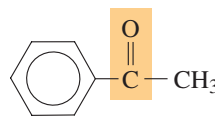
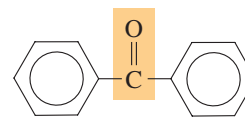
methyl ethyl ketone



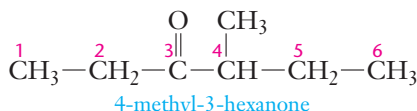
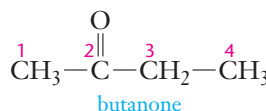
diethyl ketone



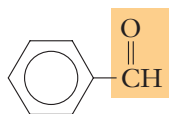
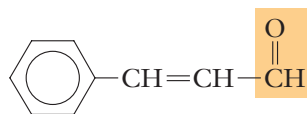
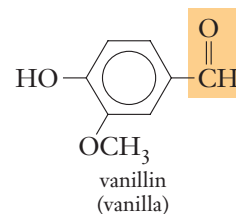
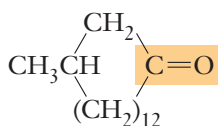
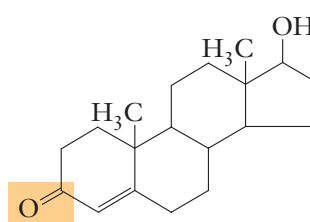
cyclohexanone

acetophenone
(methyl phenyl ketone)benzophenone
(diphenyl ketone)

The systematic names for ketones are derived from their parent hydrocarbons. The suffix *-one* is added to the characteristic stem.



The ketones are excellent solvents. Acetone is very useful because it dissolves most organic compounds yet is miscible with water. Acetone is widely used as a solvent in the manufacture of lacquers, paint removers, explosives, plastics, drugs, and disinfectants. Some ketones of high molecular weight are used extensively in blending perfumes. Structures of some naturally occurring aldehydes and ketones are

benzaldehyde
(almonds)cinnamaldehyde
(cinnamon)vanillin
(vanilla)muscone
(musk deer, used
in perfumes)testosterone
(male sex hormone)

camphor

Steroid molecules have similar molecular shapes but different biochemical functions. Progesterone (top), a female sex hormone, and testosterone (bottom), a male sex hormone. Both are ketones.

Table 23-10 Boiling Points of Ammonia and Some Amines

Name	Formula	Boiling Point (°C)
ammonia	NH ₃	−33.4
methylamine	CH ₃ NH ₂	−6.5
dimethylamine	(CH ₃) ₂ NH	7.4
trimethylamine	(CH ₃) ₃ N	3.5
ethylamine	CH ₃ CH ₂ NH ₂	16.6
aniline	C ₆ H ₅ NH ₂	184
ethylenediamine	H ₂ NCH ₂ CH ₂ NH ₂	116.5
pyridine	C ₅ H ₅ N	115.3
pyrrole	C ₄ H ₅ N	129.8

► Ammonia acts as a Lewis base because there is one unshared pair of electrons on the N atom (see Section 10-10).

23-12 Amines

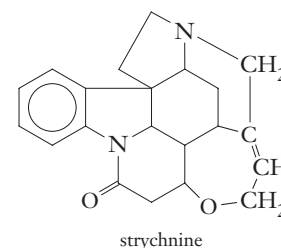
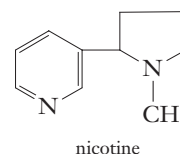
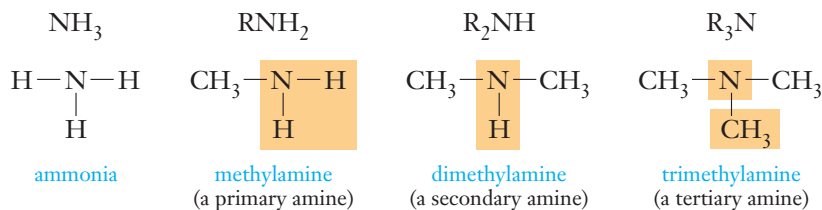
The **amines** are derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. Many low-molecular-weight amines are gases or low-boiling liquids (Table 23-10). Amines are basic compounds (see Table 18-6 and Section 24-4). The aliphatic amines of low molecular weight are soluble in water. Aliphatic diamines of fairly high molecular weight are soluble in water because each molecule contains two highly polar —NH₂ groups that form hydrogen bonds with water.

The odors of amines are quite unpleasant; many of the malodorous compounds that are released as fish decay are low-molecular-weight amines. Amines of high molecular weight are nonvolatile, so they have little odor. One of the materials used to manufacture nylon, hexamethylenediamine, is an aliphatic amine. Many aromatic amines are used to prepare organic dyes that are widely used in industrial societies. Amines are also used to produce many medicinal products, including local anesthetics and sulfa drugs.

Amines are widely distributed in nature in the form of amino acids and proteins, which are found in all higher animal forms, and in alkaloids, which are found in most plants. Some of these substances are fundamental building blocks of animal tissue, and minute amounts of others have dramatic physiological effects, both harmful and beneficial. Countless other biologically important substances, including many vitamins, antibiotics, and other drugs, contain **amino groups**, —NR₂ (where R can represent an H, alkyl, or aryl group).

Structure and Nomenclature

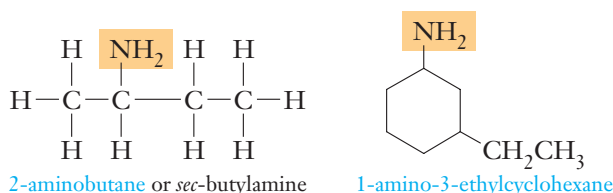
There are three classes of amines, depending on whether one, two, or three hydrogen atoms have been replaced by organic groups. They are called **primary**, **secondary**, and **tertiary amines**, respectively.



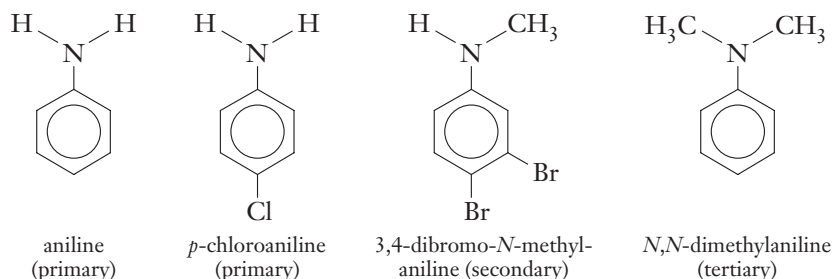
The systematic names of amines are based on consideration of the compounds as derivatives of ammonia. Amines of more complex structure are sometimes named as

Unless otherwise noted, all content on this page is © Cengage Learning.

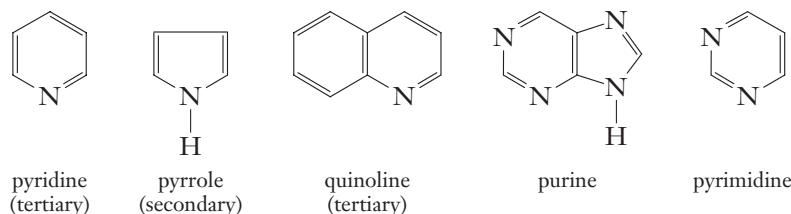
derivatives of the parent hydrocarbon with the term *amino-* used as a prefix to describe —NH_2 .



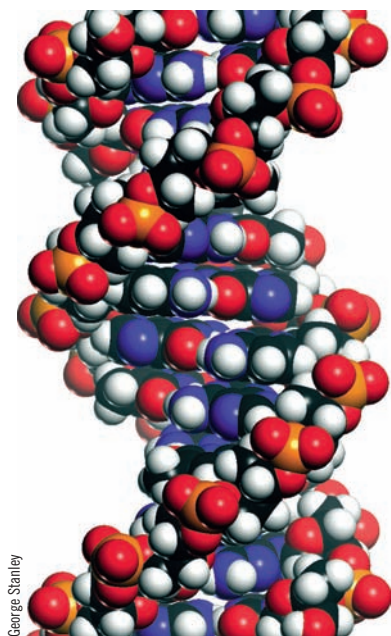
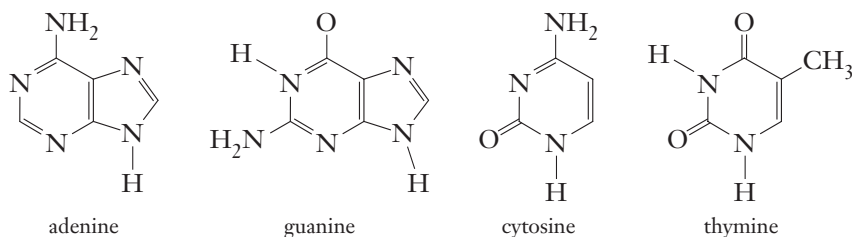
Aniline is the simplest aromatic amine. Many aromatic amines are named as derivatives of aniline.



Heterocyclic amines contain nitrogen as a part of the ring, bound to two carbon atoms. Many of these amines are found in coal tar and a variety of natural products. Some aromatic and heterocyclic amines are called by their common names.



Genes, the units of chromosomes that carry hereditary characteristics, are long stretches of double helical deoxyribonucleic acid, or DNA. DNA is composed of four *nucleotide bases*: adenine, guanine, cytosine, and thymine. The first two are modified purines, and the latter two are modified pyrimidines. The sequence of these building blocks in DNA acts as a code for the order of amino acids in the proteins of an organism. The DNA in each cell of an organism contains the instructions for making the complete organism (see Section 24-10).



George Stanley
A space-filling model of a portion of the DNA double helical structure.

23-13 Carboxylic Acids

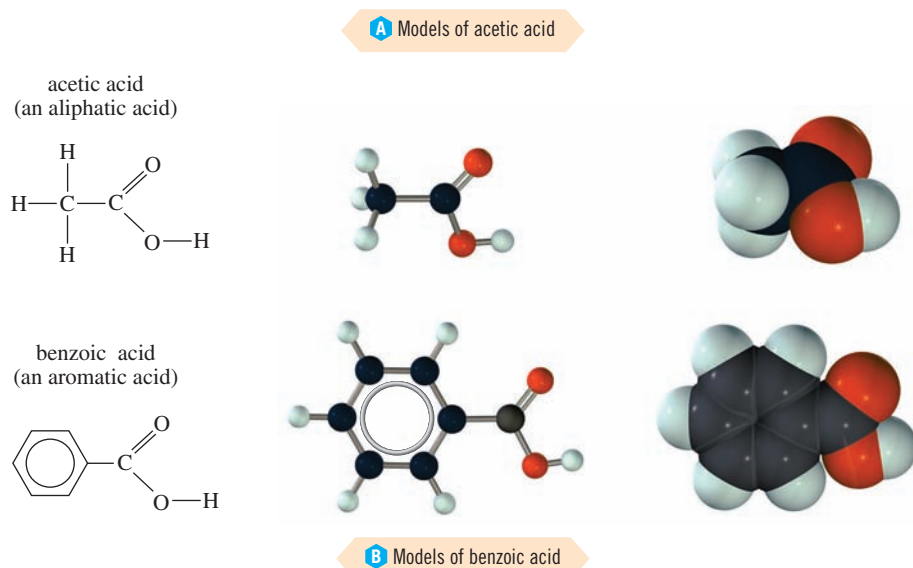
► In the general formulas for alcohols and ethers, R cannot be H. In carboxylic acids, R can be H.

Compounds that contain the **carboxyl group**, $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—O—H}$, are acidic. They are called **carboxylic acids**. Their general formula is R—COOH . Most are *weak acids*. They are much stronger acids than most phenols, however. Carboxylic acids are named systemati-

Table 23-11 Some Aliphatic Carboxylic Acids

Formula	Common Name	IUPAC Name
HCOOH	formic acid	methanoic acid
CH ₃ COOH	acetic acid	ethanoic acid
CH ₃ CH ₂ COOH	propionic acid	propanoic acid
CH ₃ CH ₂ CH ₂ COOH	butyric acid	butanoic acid
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ COOH	caproic acid	hexanoic acid
CH ₃ (CH ₂) ₁₀ COOH	lauric acid	dodecanoic acid
CH ₃ (CH ₂) ₁₄ COOH	palmitic acid	hexadecanoic acid
CH ₃ (CH ₂) ₁₆ COOH	stearic acid	octadecanoic acid

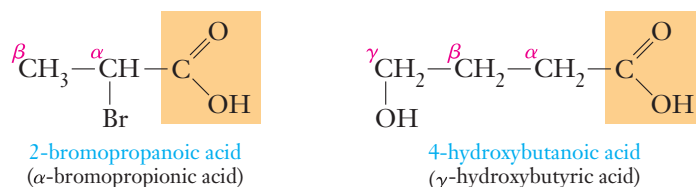
► Formic acid was obtained by distillation of ants (L. *formica*, “ant”); acetic acid occurs in vinegar (L. *acetum*, “vinegar”); butyric acid in rancid butter (L. *butyrum*, “butter”); and stearic acid in animal fats (Gr. *stear*, “beef suet”). Caproic acid is one of the so-called “goat acids.” Its odor is responsible for the name.

**Figure 23-17** Models of some carboxylic acids.

cally by dropping the terminal *-e* from the name of the parent hydrocarbon and adding *-oic acid* (Table 23-11). Many older names survive, however, and organic acids are often called by common names. In aromatic acids, the carboxyl group is attached to an aromatic ring (Figure 23-17).

Organic acids occur widely in natural products, and many have been known since ancient times. Their common (trivial) names are often derived from a Greek or Latin word that indicates the original source (see Table 23-11).

The names of modified carboxylic acids are often derived from the trivial names of the acids. Positions of substituents are sometimes indicated by lowercase Greek letters, beginning with the carbon *adjacent* to the carboxyl carbon, rather than by numbering the carbon chain.



► Long-chain aliphatic carboxylic acids are often referred to as *fatty acids* because many have been obtained from animal fats.

► Derivatives of α -hydroxy carboxylic acids are currently used in some cosmetic preparations.

The Chemistry of Artists' Pigments

In a way, every great masterpiece of art is also a great masterpiece of chemistry: in the technique of painting, an artist's ideas are expressed by the application of pigments in a certain arrangement on a canvas. And what are pigments but chemical compounds of a particularly pleasing color? In fact, from the earliest known natural colorants to modern synthetic dyes, the science of paints has played an important role in the development of chemistry.

Naturally occurring inorganic pigments have been known since ancient times. Iron and manganese oxides (referred to by modern artists as red earths, ochers, umbers, and siennas) have been found in cave paintings. Artists in Egypt, China, and classical civilizations used the mineral colorants azurite (blue, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), realgar (red, AsS), cinnabar (vermilion, HgS), chalk (white, CaCO_3), baryte (white, BaSO_4), and orpiment (yellow, As_2S_3). Simple chemical processes such as calcination or oxidation were used to isolate other pigments, such as Naples yellow ($\text{Pb}(\text{SbO}_3)_2$), Egyptian blue (a calcium copper silicate, $\text{CuO} \cdot \text{CaO} \cdot \text{SiO}_2$), and verdigris (copper acetate monohydrate).

A few pigments used before modern times were derived from natural organic sources. Indigo and madder come from plants, while carmine and sepia are isolated from cochineal insects and cuttlefish ink, respectively. Natural organic pigments are not very permanent, however, and most have been replaced with superior synthetic substitutes. One exception is the family of charcoals resulting from carbonization of animal or vegetable remains (referred to as lamp black, bone black, and ivory black). These pigments are still used widely today.

Beginning with the Industrial Revolution in the eighteenth century, many synthetic inorganic pigments have added to or replaced natural mineral colorants as artists' materials. These pigments offer advantages of permanence, opacity, novelty of color, or consistency (for example, natural baryte is often discolored pink or yellow by manganese or iron mineral inclusions, while the synthetic variety is pure white). One of the earliest synthetic pigments is Prussian blue (ferric ferrocyanide, $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$), first prepared in 1704. Chromates, oxides, and other simple salts have also found widespread use as colorants and are typically named according to their tint and the metal cation incorporated. Barium yellow (BaCrO_4), chrome red ($\text{PbCrO}_4 \cdot \text{Pb}(\text{OH})_2$), Mars black (FeO), Chinese white (ZnO), cadmium orange (CdS), viridian green ($\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), and Cerulean blue (CoSnO_3) are examples of such pigments.

Artists' pigments do not lose their chemical identities once they are fixed on a canvas. While the use of paint varnishes may protect them from the atmosphere to some degree, colorants can still undergo the chemical reactions characteristic of their structures. Flake white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) and other lead-containing pigments react with the H_2S fumes in smoggy city air to form black lead sulfide, PbS , resulting in an undesirable darkening. Oxide- and sulfide-containing pigments may also decompose by reacting with atmospheric CO_2 to form metal carbonates. Chemical reactions with the human body are also unaffected, and for this reason paints containing arsenic, lead, cadmium, and mercury are considered toxic (the term "painters' colic" refers to lead poisoning from pigment inhalation or ingestion).

Unless otherwise noted, all content on this page is © Cengage Learning.



Jan Cook/Getty Images

Raw pigments are powders of colored organic or inorganic compounds.



Golden Artist Colors, Inc.

A milling machine mixes pigments with light oils to produce oil paint. Pigments in paints usually do not dissolve, but rather are very finely dispersed into oil or another liquid.

Over the last century, new classes of synthetic organic colorants have been developed that are more permanent than natural organic pigments. Some "organic" synthetics are metallic compounds containing organic ligands, such as phthalocyanine blue and green (known as "Thalo" or Monastral), developed in the 1920s. These pigments are copper(II) compounds that incorporate a complex, cyclic organic fragment as the anion. Other synthetics are purely organic species that happen to absorb light in the visible region due to their structures. Alizarin (1,2-dihydroxyanthraquinone, synthetic madder) and quinacridone pigments belong to this class of colorants.

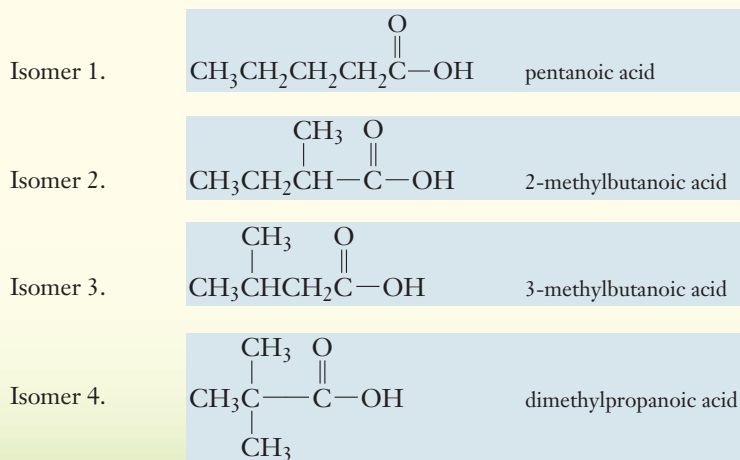
LISA SAUNDERS BAUGH

EXAMPLE 23-12 Isomeric Carboxylic Acids

Write the structural formula of each of the four carboxylic acids having the molecular formula of $C_5H_{10}O_2$. Give the IUPAC name of each.

Plan

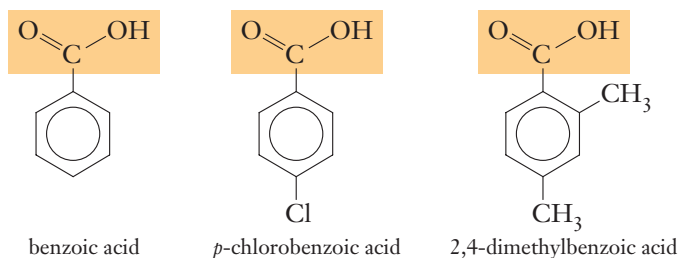
We first write the structural formula of the carboxylic acid that does not have branching. Then we remove one carbon from the straight-chain structure and reposition it to form branched isomers. We check to see whether branching is possible at more than one location. We find that branching is possible at two different locations. Remove a second carbon and, if possible, form additional branching. The two removed carbons can be added as methyl branches. Each isomer is named by naming the longest chain that contains the carboxylic acid group. The final *-e* of the name is changed to *-oic acid*. Names for branches appear at the beginning of the name.

Solution

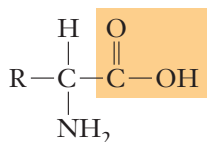
You should now work Exercise 72a, b.

Some carboxylic acid molecules contain more than one $-\text{COOH}$ group (Table 23-12). These acids are nearly always called by their common names. For example, oxalic acid, found in rhubarb, spinach, and tomatoes, is a dicarboxylic acid; citric acid, found in citrus fruits, is a tricarboxylic acid.

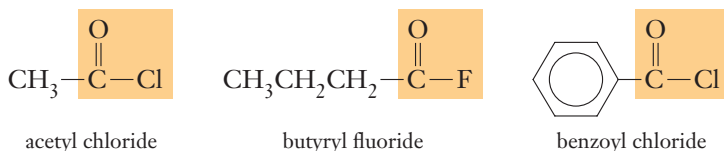
Aromatic acids are called by their common names or named as derivatives of benzoic acid, which is considered the “parent” aromatic acid.



Although many carboxylic acids occur in the free state in nature, many occur as amides or esters (Section 23-14). **α -Amino acids** are substituted carboxylic acids with the general structure



named by combining the stems of the common names of the carboxylic acids with the suffix *-yl* and then adding the name of the halide ion. Examples are

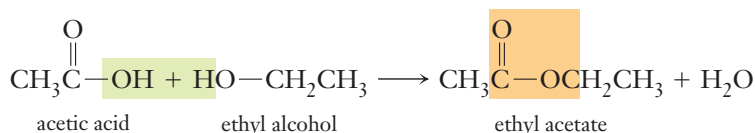


Acid halides are very reactive and have not been observed in nature.

Esters

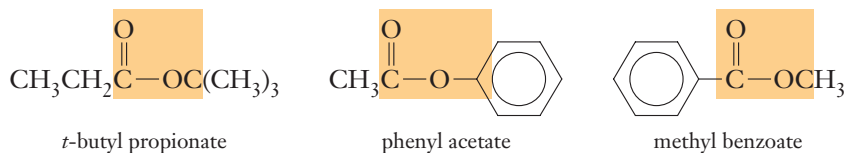
An **ester** can be thought of as the result of removing one molecule of water from a carboxylic acid and an alcohol. Removing a molecule of water from acetic acid and ethyl alcohol gives ethyl acetate.

► As we will see in Section 24-6, one method of forming esters involves an acid-catalyzed reaction of an alcohol with a carboxylic acid.



The $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C}\text{—}$ fragment is derived from acetic acid, the parent acid; the $\text{—O—CH}_2\text{CH}_3$ fragment is derived from ethanol, the parent alcohol. Models of ethyl acetate, an ester, are shown in Figure 23-18.

Esters are nearly always called by their common names. These consist of, first, the name of the alkyl group in the alcohol, and then the name of the anion derived from the acid.



Because of their inability to form hydrogen bonds, esters tend to be liquids with boiling points that are much lower than those of carboxylic acids of similar molecular weights.

Most simple esters are pleasant-smelling substances. They are responsible for the flavors and fragrances of most fruits and flowers and many of the artificial fruit flavorings that are used in cakes, candies, and ice cream (Table 23-13). Esters of low molecular weight are excellent solvents for nonpolar compounds. Ethyl acetate is an excellent solvent that gives some nail polish removers their characteristic odor.

Fats (solids) and **oils** (liquids) are esters of glycerol and aliphatic acids of high molecular weight. **Fatty acids** are long-chain organic acids whose esters occur in fats and oils. Fats and oils have the general formula

► Glycerol is

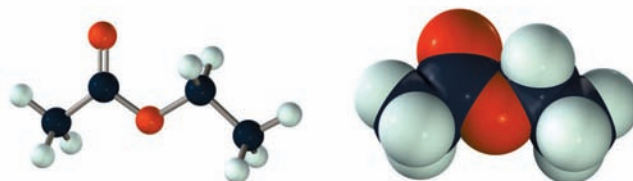
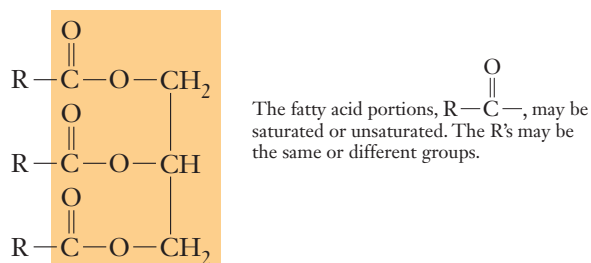
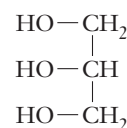
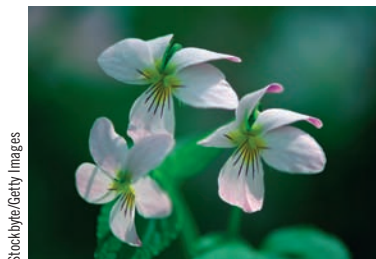


Figure 23-18 Models of ethyl acetate, $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C}\text{—O—CH}_2\text{CH}_3$, an ester.

Unless otherwise noted, all content on this page is © Cengage Learning.



Apple blossoms.

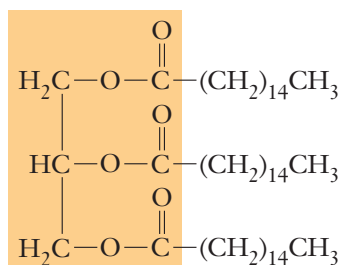
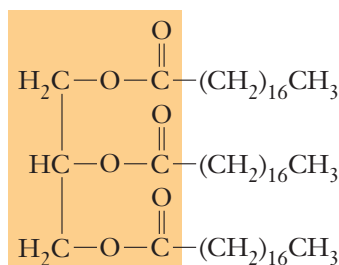
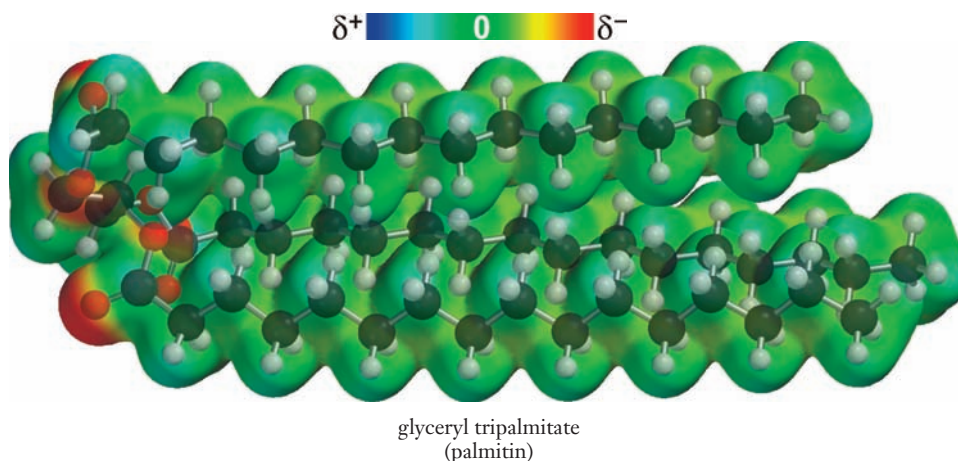
Table 23-13 Some Common Esters

Ester	Formula	Odor of
isoamyl acetate	$\text{CH}_3\text{COOC}_5\text{H}_{11}$	bananas
ethyl butyrate	$\text{C}_3\text{H}_7\text{COOC}_2\text{H}_5$	pineapples
amyl butyrate	$\text{C}_3\text{H}_7\text{COOC}_5\text{H}_{11}$	apricots
octyl acetate	$\text{CH}_3\text{COOC}_8\text{H}_{17}$	oranges
isoamyl isovalerate	$\text{C}_4\text{H}_9\text{COOC}_5\text{H}_{11}$	apples
methyl salicylate	$\text{C}_6\text{H}_4(\text{OH})(\text{COOCH}_3)$	oil of wintergreen
methyl anthranilate	$\text{C}_6\text{H}_4(\text{NH}_2)(\text{COOCH}_3)$	grapes

Naturally occurring fats and oils are mixtures of many different esters. Milk fat, lard, and tallow are familiar, important fats. Soybean oil, cottonseed oil, linseed oil, palm oil, and coconut oil are examples of important oils.

The triesters of glycerol are called **glycerides**. Many glycerides are symmetrical esters in which all three R groups are identical. Two examples are

► Most natural fatty acids contain even numbers of carbon atoms because they are synthesized in the body from two-carbon acetyl groups.

glyceryl tripalmitate
(palmitin)glyceryl tristearate
(stearin)

Waxes are esters of fatty acids and alcohols other than glycerol. Most are derived from long-chain fatty acids and long-chain monohydric alcohols. Both usually contain even numbers of carbon atoms. Beeswax is largely $\text{C}_{15}\text{H}_{31}\text{COOC}_{30}\text{H}_{61}$; carnauba wax contains $\text{C}_{25}\text{H}_{51}\text{COOC}_{30}\text{H}_{61}$. Both are esters of myricyl alcohol, $\text{C}_{30}\text{H}_{61}\text{OH}$.

Fats are solid esters of glycerol and (mostly) saturated acids. Oils are liquid esters that are derived primarily from unsaturated acids and glycerol. The acid portion of a fat usually contains an even number of carbon atoms, often 16 or 18. Some acids that occur frequently in fats and oils are

butyric	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
lauric	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
myristic	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$

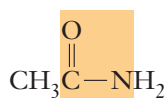
palmitic	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
stearic	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
oleic	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
linolenic	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
ricinoleic	$\text{CH}_3(\text{CH}_2)_5\text{CHOHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$

Figure 23-19a shows a model of stearic acid, a long-chain saturated fatty acid.

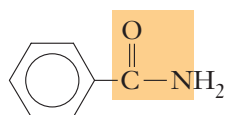
Amides

Amides are thought of as derivatives of organic acids and ammonia, primary amines, or

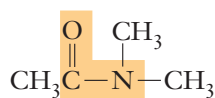
secondary amines. Amides contain the $\text{—}\overset{\text{O}}{\parallel}\text{C—N—}$ functional group. They are named as derivatives of the corresponding carboxylic acids, the suffix *-amide* being substituted for *-ic acid* or *-oic acid* in the name of the parent acid. The presence of alkyl or aryl substituents attached to nitrogen is designated by prefixing the letter *N* and the name of the substituent to the name of the unsubstituted amide.



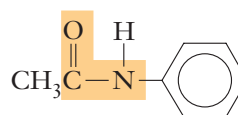
acetamide



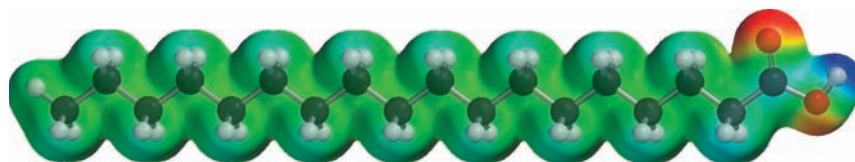
benzamide



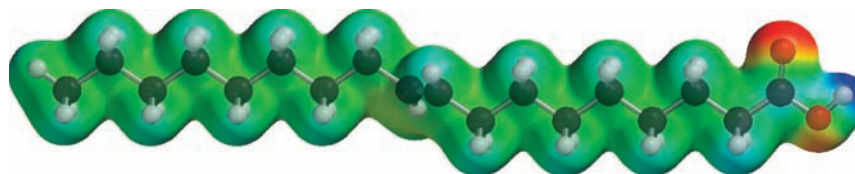
N,N-dimethylacetamide



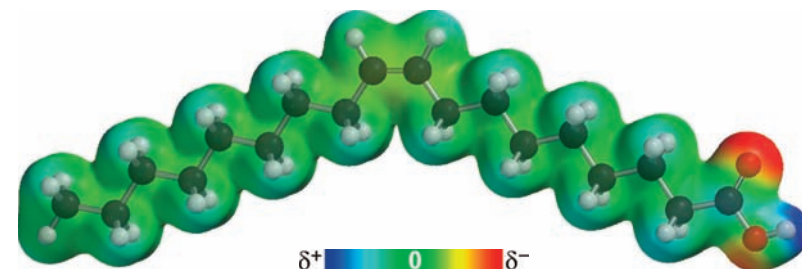
N-phenylacetamide
(acetanilide)



A Stearic acid, $\text{C}_{17}\text{H}_{35}\text{COOH}$. Saturated fatty acids are linear and tend to pack like sticks of wood to form solid masses in blood vessels, thereby constricting them.



B *trans*-Oleic acid, $\text{C}_{17}\text{H}_{33}\text{COOH}$. *Trans* unsaturated fatty acids have a slight Z-shaped kink in the chain but are also essentially linear molecules.



C *cis*-Oleic acid, $\text{C}_{17}\text{H}_{33}\text{COOH}$. By contrast, *cis* unsaturated fatty acids are bent and so do not pack as well as linear structures and do not collect in blood vessels as readily. Many natural vegetable fats and oils contain esters of *cis* unsaturated fatty acids, or polyunsaturated fatty acids. Health problems associated with saturated fatty acids can be decreased by eating less animal fat, butter, and lard. Problems due to *trans* fatty acids are reduced by avoiding processed vegetable fats.

Figure 23-19 Models of long-chain fatty acids.



Honeybees produce the wax to build their honeycombs.

CHEMISTRY IN USE

Butter, Margarine, and *trans* Fats

Humans had consumed butter for thousands of years before France introduced the world to margarine in the late 1860s; by 1874, margarine had reached the United States. Margarine consumption has increased rapidly, due in part to an increased risk of heart disease that has been associated with consumption of butter.

Both butter and margarine are primarily fats, but they contain different kinds of fats. The main ingredient in butter is cream, the concentrated fat from milk, whereas the main ingredient in margarine is vegetable oil, the concentrated fat from plants. Although it is widely accepted that animal fats pose a greater risk for heart disease than vegetable oils, most vegetable oils used in margarine and processed foods are modified by hydrogenation.

The hydrogenation process adds hydrogen atoms to unsaturated vegetable oils; this causes vegetable oils to solidify, which makes them creamier and prolongs their shelf life. Unfortunately, the hydrogenation process changes about 40% of the naturally occurring *cis* molecules of vegetable oil into *trans* isomers; the resulting fat molecules are referred to as *trans* fats. Oils produced in nature contain only *cis* isomers and are considered healthful, but the *trans* fats have been linked to many thousands of deaths due to heart disease. Diets high in hydrogenated vegetable oil may be as unhealthy as those high in saturated animal fats.

To understand the different effects produced by animal fats, vegetable oils, and *trans* fats, we need to know a little about blood cholesterol. Medical specialists recognize several types of cholesterol, two of which are HDL (high-density lipoproteins) and LDL (low-density lipoproteins). Because high levels of HDL reduce the risk of heart disease, HDL has become known as “good” cholesterol; because high levels of LDL increase the risk for heart disease, LDL has become known as “bad” cholesterol. In the average U.S. adult, the total amount of cholesterol (including HDL and LDL) circulating in the blood is about 200 mg per 100 mL of serum.

A diet high in animal fats usually increases blood cholesterol levels beyond 200 mg per 100 mL of serum, thereby increasing the risk for heart disease. When animal fats increase the total blood



Science VL-WHC/Visuals Unlimited

Blood pressure check.

cholesterol level, however, they increase the levels of both HDL and LDL. In contrast, vegetable oils decrease the total blood cholesterol level, which makes them healthier foods than other fats. *Trans* fats (from hydrogenated vegetable oils) also decrease the total blood cholesterol level, giving the appearance of being healthy, but unfortunately they accomplish this reduction by simultaneously reducing the desirable HDL levels and increasing the undesirable LDL levels.

The damage done by hydrogenated vegetable oils is particularly disturbing because margarine is one of the largest sources of calories in the U.S. diet; approximately 40% of margarine fat is the *trans* isomer. Hydrogenated vegetable oils are widely used in shortening, cookies, crackers, chips, and other processed foods. Ironically, most of these foods are touted as being healthy because they contain no cholesterol or saturated fats.

What can we do to protect our health? For many years, nutritionists have been telling us what appears to be the “best solution”: reduce your total fat intake to 20% of your daily calories, and reduce your consumption of animal fats by substituting vegetable oils. Whenever possible, use vegetable oils that have not been hydrogenated.

RONALD DELORENZO

Proteins are complex amides of high molecular weight. Some synthetic fibers are also polyamides (Section 23-19).

23-15 Summary of Functional Groups

Some important functional groups and the corresponding classes of related compounds are summarized in Figure 23-20.

Michael W. Davidson/Photo Researchers, Inc.



Crystals of the amide known as acetaminophen (Tylenol) viewed under polarized light. The structure of acetaminophen is

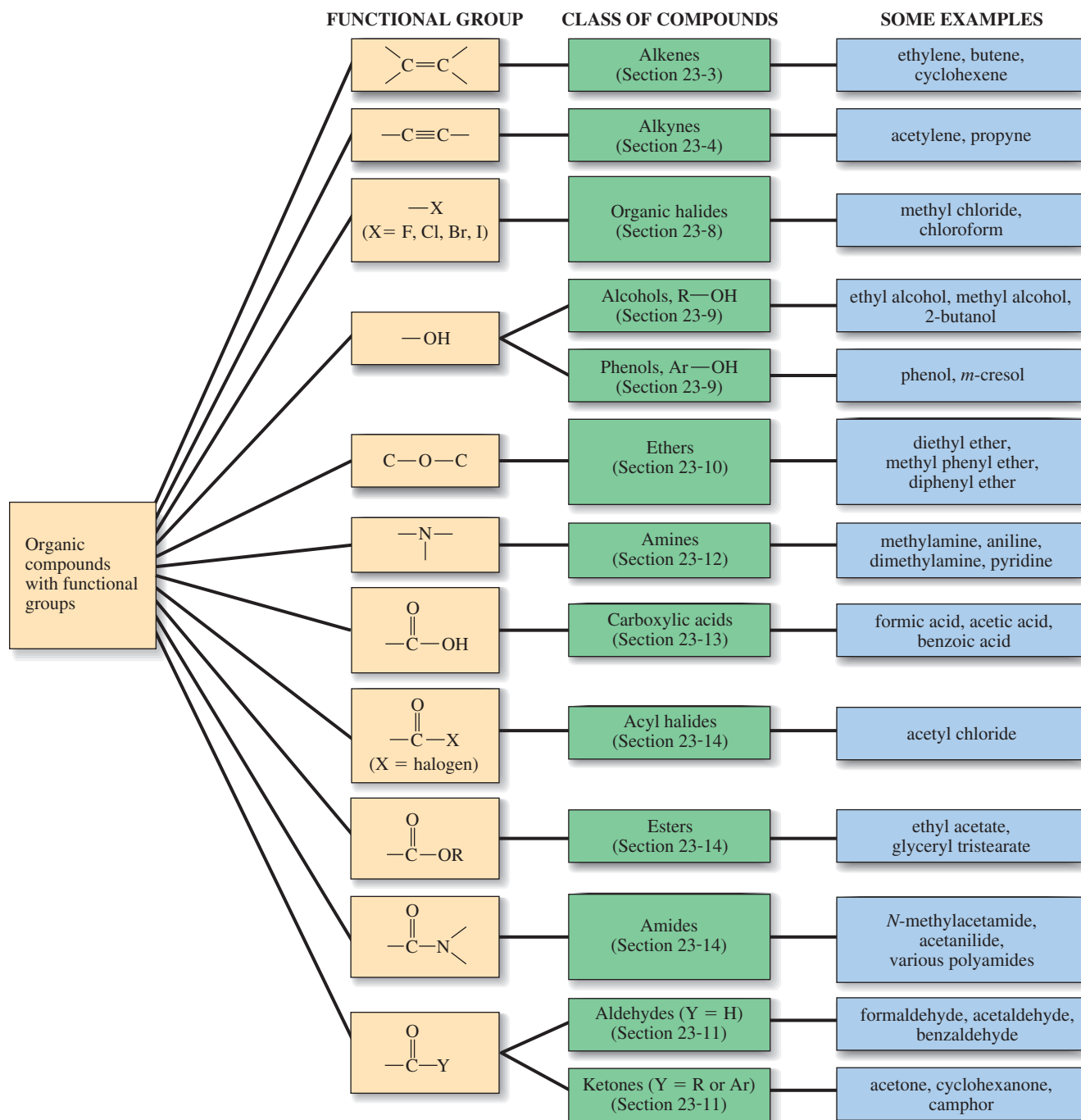
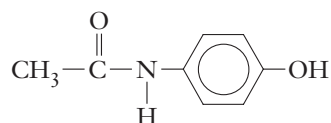


Figure 23-20 Summary of some functional groups and classes of organic compounds.

Unless otherwise noted, all content on this page is © Cengage Learning.

Fundamental Classes of Organic Reactions

Organic compounds display very different abilities to react, ranging from the limited reactivity of hydrocarbons and fluorocarbons to the great variety of reactions undergone by the millions of organic molecules that contain several functional groups. Reactivity depends on structure. We can usually predict the kinds of reactions a compound can undergo by identifying the functional groups it contains. But the electronic and structural features that are *near* a functional group can also affect its reactivity. One of the fascinations of organic chemistry is our ability to “fine-tune” both physical and chemical properties by making small changes in structure. The successes of this approach are innumerable, including the development of fuels and their additives or alternatives, the improvement of pharmaceuticals to enhance their effectiveness and minimize their ill effects, and the development of polymers and plastics with an incredible variety of properties and uses.

In the following sections of this chapter, we will present a few of the kinds of reactions that organic compounds undergo. A topic of such vast scope as reactivity of organic compounds can be made manageable only if we divide our study into subtopics. Nearly all organic transformations involve at least one of three fundamental classes of reactions. The following three sections will address substitution, addition, and elimination reactions. We will also look at some reaction sequences that combine reaction steps from more than one of the fundamental classes.

23-16 Substitution Reactions

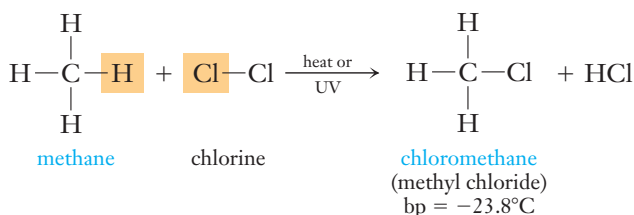
In a **substitution reaction**, an atom or a group of atoms attached to a carbon atom is removed, and another atom or group of atoms takes its place. No change occurs in the degree of saturation at the reactive carbon atom.

► The term “paraffin” comes from the Latin *parum* “barely” + *affinis* “related” – referring to their low reactivity or affinity for other compounds.

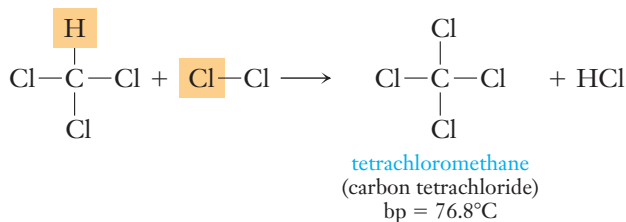
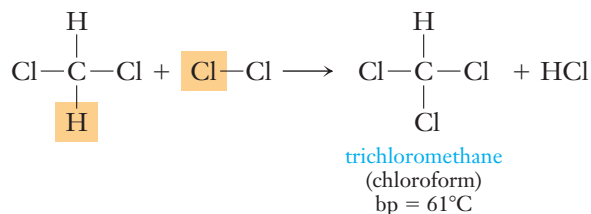
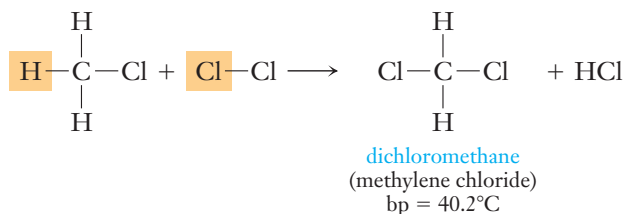
The saturated hydrocarbons (alkanes and cycloalkanes) are chemically rather inert materials. For many years, they were known as *paraffins* because they undergo few reactions. They do not react with such powerful oxidizing agents as potassium permanganate and potassium dichromate. They do, however, react with the halogens, with oxygen when ignited, and with concentrated nitric acid. As expected, members of a homologous series (Section 23-1) have similar chemical properties. If we study the chemistry of one of these compounds, we can make predictions about the others with a fair degree of certainty.

The saturated hydrocarbons can react without a big disruption of the molecular structure only by *displacement*, or *substitution of one atom for another*. At room temperature, chlorine and bromine react very slowly with saturated straight-chain hydrocarbons. At higher temperatures, or in the presence of sunlight or other sources of ultraviolet light, H atoms in the hydrocarbon can be replaced easily by halogen atoms. These substitution reactions are called **halogenation reactions**.

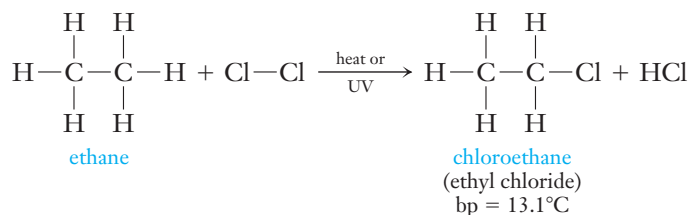
The reaction is represented as



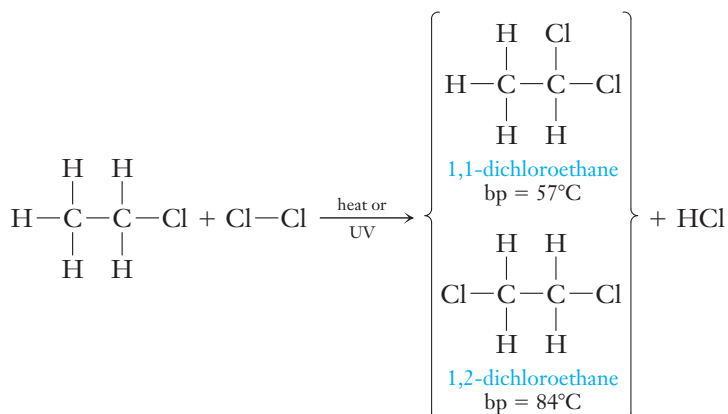
Many organic reactions produce more than a single product. For example, the chlorination of CH_4 may produce several other products in addition to CH_3Cl , as the following equations show.



When a hydrocarbon has more than one C atom, its reaction with Cl_2 is more complex. The first step in the chlorination of ethane gives the product that contains one Cl atom per molecule.



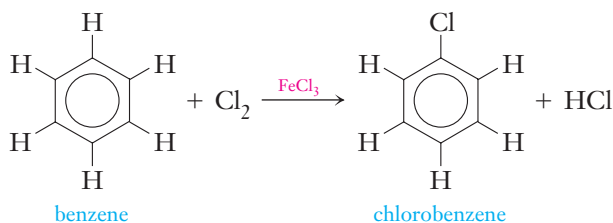
When a second hydrogen atom is replaced, a mixture of the two possible products is obtained.



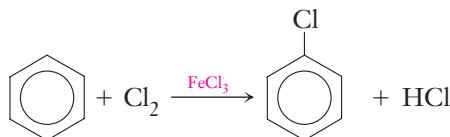
► The product mixture does not contain equal numbers of moles of the dichloroethanes, so we do not show a stoichiometrically balanced equation. Because reactions of saturated hydrocarbons with chlorine can produce many products, the reactions are not always as useful as might be desired.

Substitution is the most common kind of reaction of an aromatic ring. Halogenation with chlorine or bromine occurs readily in the presence of iron or anhydrous iron(III) chloride (a Lewis acid) catalyst.

► When iron is added as a catalyst, it reacts with chlorine to form iron(III) chloride, which is the true catalyst.

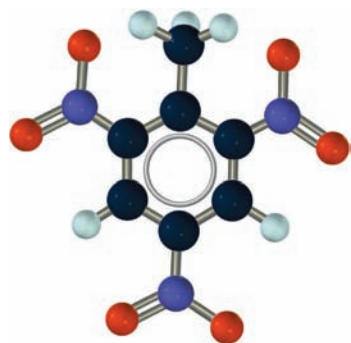
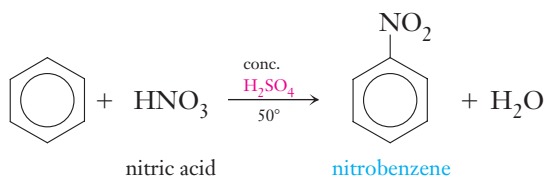


The equation is usually written in condensed form as



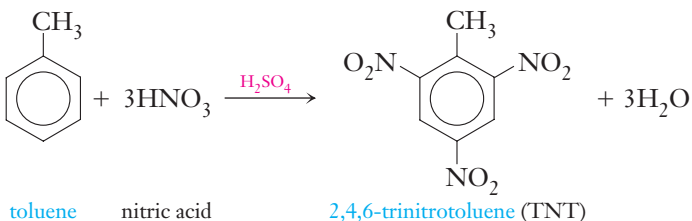
Aromatic rings can undergo *nitration*, substitution of the *nitro* group —NO₂, in a mixture of concentrated nitric and sulfuric acids at moderate temperatures.

► The H₂SO₄ is both a catalyst and a dehydrating agent. The H in the product H₂O comes from the hydrocarbon; the OH comes from HNO₃.

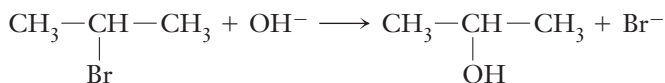


A model of a molecule of TNT.

The explosive TNT (2,4,6-trinitrotoluene) is manufactured by the nitration of toluene in three steps.

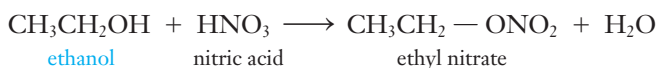


Groups other than hydrogen can be substituted by other atoms or groups of atoms. For example, the bromine atom of an alkyl bromide can be replaced with a hydroxyl group to form an alcohol. The mechanism of this type of reaction is often studied in introductory organic chemistry courses.



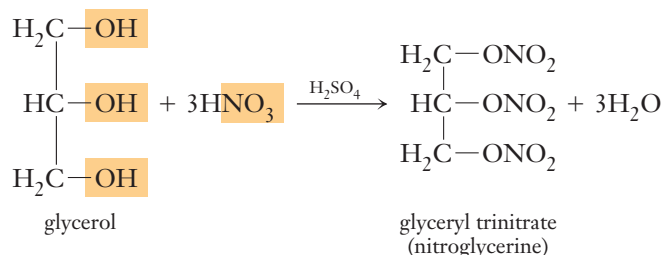
► Simple inorganic esters may be thought of as compounds that contain one or more alkyl groups covalently bonded to the anion of a *ternary* inorganic acid. Unless indicated, the term “ester” refers to organic esters.

Alcohols react with common inorganic oxyacids to produce **inorganic esters**. For instance, nitric acid reacts with alcohols to produce nitrates by substitution of nitrate, —ONO₂, for hydroxyl, —OH.



Unless otherwise noted, all content on this page is © Cengage Learning.

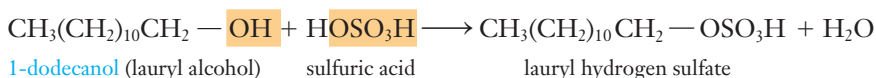
The substitution reaction of nitric acid with glycerol produces the explosive nitroglycerine. Alfred Nobel's (1833–1896) discovery in 1866 that this very sensitive material could be made into a “safe” explosive by absorbing it into diatomaceous earth or wood meal led to his development of dynamite.



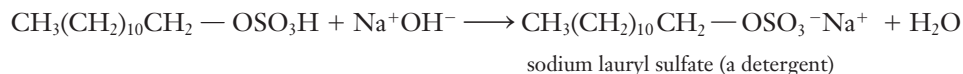
► Nobel's brother had been killed and his father physically disabled in a nitroglycerine explosion in 1864. Nobel willed \$9.2 million to establish a fund for annual prizes in physics, chemistry, medicine, literature, and peace. The prizes were first awarded in 1901.

► Interestingly, nitroglycerine (“nitro”) is taken by some who have heart disease. It releases small amounts of nitrogen oxide, NO, which act as a vasodilator (dilates the blood vessels) to decrease arterial tension.

Cold, concentrated H_2SO_4 reacts with alcohols to form **alkyl hydrogen sulfates**. The reaction with lauryl alcohol is an important industrial reaction.



The neutralization reaction of an alkyl hydrogen sulfate with NaOH then produces the sodium salt of the alkyl hydrogen sulfate.

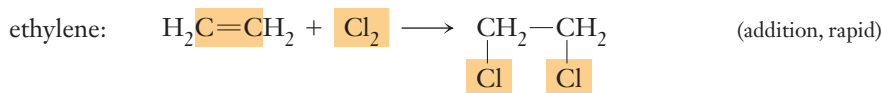
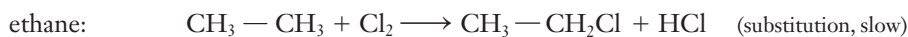


Sodium salts of the alkyl hydrogen sulfates that contain about 12 carbon atoms are excellent detergents. They are also biodegradable. (Soaps and detergents were discussed in Section 14-18.)

23-17 Addition Reactions

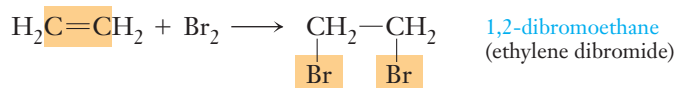
An **addition reaction** involves an *increase* in the number of atoms or groups attached to carbon. The molecule becomes more nearly saturated.

The principal reactions of alkenes and alkynes are addition reactions rather than substitution reactions. For example, contrast the reactions of ethane and ethylene with Cl_2 .



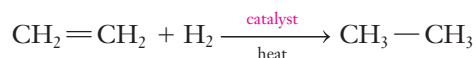
Carbon-carbon double bonds are *reaction sites* and so represent *functional groups*. Most addition reactions involving alkenes and alkynes proceed rapidly at room temperature. By contrast, many substitution reactions of the alkanes require catalysts and high temperatures.

Bromine adds readily to the alkenes to give dibromides. The reaction with ethylene is



The addition of Br_2 to alkenes is used as a simple qualitative test for unsaturation. Bromine, a dark red liquid, is dissolved in a nonpolar solvent. When an alkene is added, the solution becomes colorless as the Br_2 reacts with the alkene to form a colorless compound. This reaction may be used to distinguish between alkanes and alkenes.

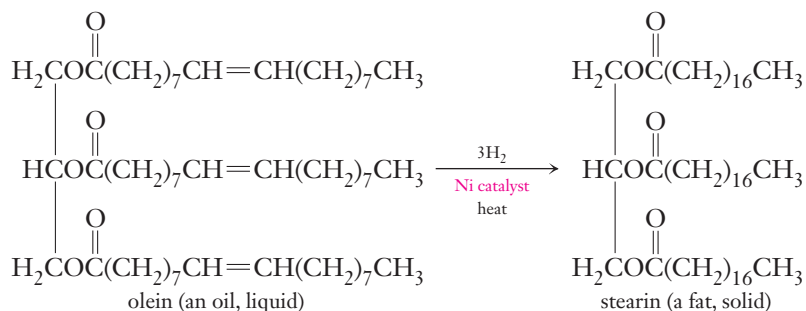
Hydrogenation is an extremely important addition reaction of the alkenes. Hydrogen adds across double bonds at elevated temperatures, under high pressures, and in the presence of an appropriate catalyst (finely divided Pt, Pd, or Ni).



Some unsaturated hydrocarbons are converted to saturated hydrocarbons in the manufacture of high-octane gasoline and aviation fuels. Unsaturated vegetable oils can also be converted to solid cooking fats (shortening) by hydrogenation of most of the carbon-carbon double bonds present (Figure 23-21). Most of the double bonds that remain are the *trans* isomer.



Figure 23-21 Hydrogenation of the olefinic double bonds in vegetable oil converts it to solid fat.



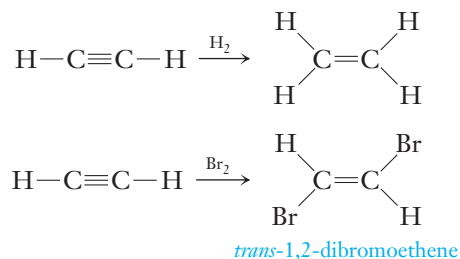
The **hydration reaction** (addition of water) is another very important addition reaction of alkenes. It is used commercially for the preparation of a wide variety of alcohols from petroleum by-products. Ethanol, the most important industrial alcohol, is produced by the hydration of ethylene from petroleum, using H_2SO_4 as a catalyst.

► Think of H_2O as HOH .



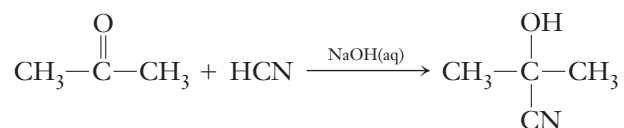
One of the commercially most important addition reactions of the alkenes forms *polymers*. This reaction will be discussed in Section 23-19.

The alkynes contain two pi bonds, both of which are sources of electrons, and they are more reactive than the alkenes. The most common reaction of the alkynes is addition across the triple bond. The reactions with hydrogen and with bromine are typical.



Other unsaturated bonds can also undergo addition reactions. Probably the most

important example is the carbonyl group, $\text{C}=\text{O}$. Because of the availability of unshared pairs of electrons on the oxygen atom, the products can undergo a wide variety of subsequent reactions. For example, HCN adds to the $\text{C}=\text{O}$ bond of acetone.

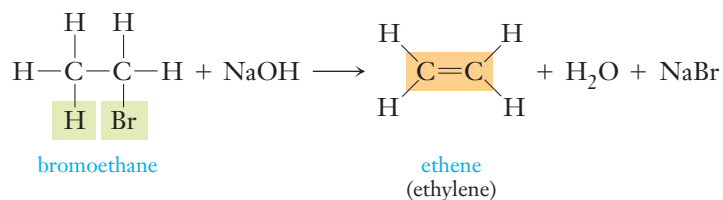


This reaction is a key early step in the production of the transparent plastic known as Plexiglas or Lucite.

23-18 Elimination Reactions

An **elimination reaction** involves a *decrease* in the number of atoms or groups attached to carbon. The degree of unsaturation increases.

An elimination reaction, **dehydrohalogenation**, can occur for chloro-, bromo-, and iodoalkanes. In such a reaction, the halogen, X, from one C atom and a hydrogen from an adjacent C atom are eliminated. A double bond between two carbon atoms is formed; the molecule becomes *more unsaturated*. The net reaction is the transformation of an alkyl halide (or haloalkane) into an alkene. Dehydrohalogenation reactions usually require a strong base such as sodium hydroxide, NaOH.



A related reaction is **dehydration**, in which an alcohol is converted into an alkene and water by the elimination of H— and —OH from adjacent carbon atoms. The



Concentrated sulfuric acid is an excellent dehydrating agent. Here it removes water from sucrose, a sugar with the formula $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. Dehydration of sucrose produces large amounts of carbon and heat.

Unless otherwise noted, all content on this page is © Cengage Learning.

dehydration of an alcohol to form an alkene can be considered the reverse of the hydration of an alkene to form an alcohol (Section 23-17). Dehydration reactions are catalyzed by acids.

Such simple elimination reactions are relatively rare. Elimination reactions, however, frequently occur as individual steps in more complex reaction sequences. Many more elimination reactions are encountered in courses in organic chemistry.

23-19 Polymerization Reactions

► The word fragment *-mer* means “part.” Recall that *isomers* are compounds that are composed of the same (*iso*) parts (*mers*). A *monomer* is a “single part”; a large number of monomers combine to form a *polymer*, “many parts.”

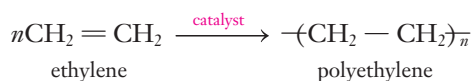
A **polymer** is a large molecule that is a high-molecular-weight chain of small molecules. The small molecules that are linked to form polymers are called **monomers**. Typical polymers consist of hundreds or thousands of monomer units and have molecular weights up to thousands or millions.

Polymerization is the combination of many small molecules (monomers) to form large molecules (polymers).

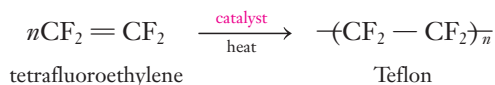
Polymers are divided into two classes: natural and synthetic. Important biological molecules such as proteins, nucleic acids, and polysaccharides (starches and the cellulose in wood and cotton) are natural polymers. Natural rubber and natural fibers such as silk and wool are also natural polymers. Familiar examples of synthetic polymers include plastics such as polyethylene, Teflon, and Lucite (Plexiglas) and synthetic fibers such as nylon, Orlon, and Dacron. In this section, we will describe some processes by which polymers are formed from organic compounds.

Addition Polymerization

Polymerization is an important addition reaction (Section 23-17) of the alkenes. Polymers formed by this kind of reaction are called **addition polymers**. The formation of polyethylene is an important example. In the presence of appropriate catalysts (a mixture of aluminum trialkyls, R_3Al , and titanium tetrachloride, $TiCl_4$), ethylene polymerizes into chains containing 800 or more carbon atoms.



The polymer may be represented as $CH_3(CH_2 - CH_2)_nCH_3$, where n is approximately 400. Polyethylene is a tough, flexible plastic. It is widely used as an electrical insulator and for the fabrication of such items as unbreakable refrigerator dishes, plastic cups, and squeeze bottles. Polypropylene is made by polymerizing propylene, $CH_3 - CH = CH_2$, in much the same way. Teflon is made by polymerizing tetrafluoroethylene in a similar reaction.



The molecular weight of Teflon is about 2×10^6 . Approximately 20,000 $CF_2 = CF_2$ molecules polymerize to form a single giant molecule. Teflon is a very useful polymer. It does *not* react with concentrated acids and bases or with most oxidizing agents. It does not dissolve in most organic solvents.

Natural rubber is obtained from the sap of the rubber tree, a sticky liquid called latex. Rubber is a polymeric hydrocarbon formed in the sap by the combination of about 2000 molecules of 2-methyl-1,3-butadiene, commonly called isoprene. The molecular weight of rubber is about 136,000.

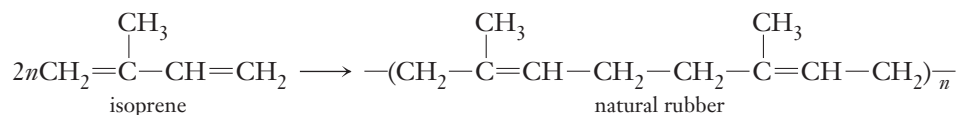
► Teflon is a trade name owned by DuPont, a company that has developed and manufactured many fluorinated polymers.



Many cooking utensils with “nonstick” surfaces are coated with a polymer such as Teflon.

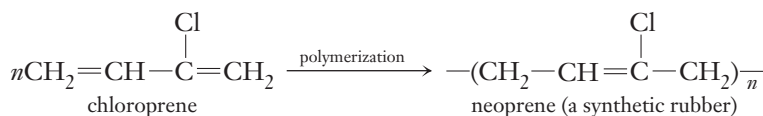
Charles D. Winters

Unless otherwise noted, all content on this page is © Cengage Learning.



When natural rubber is warmed, it flows and becomes sticky. To eliminate this problem, **vulcanization** is used. This is a process in which sulfur is added to rubber and the mixture is heated to approximately 140°C. Sulfur atoms combine with some of the double bonds in the linear polymer molecules to form bridges that bond one rubber molecule to another. This cross-linking by sulfur atoms converts the linear polymer into a three-dimensional polymer. Fillers and reinforcing agents are added during the mixing process to increase the durability of rubber and to form colored rubber. Carbon black is the most common reinforcing agent. Zinc oxide, barium sulfate, titanium dioxide, and antimony(V) sulfide are common fillers.

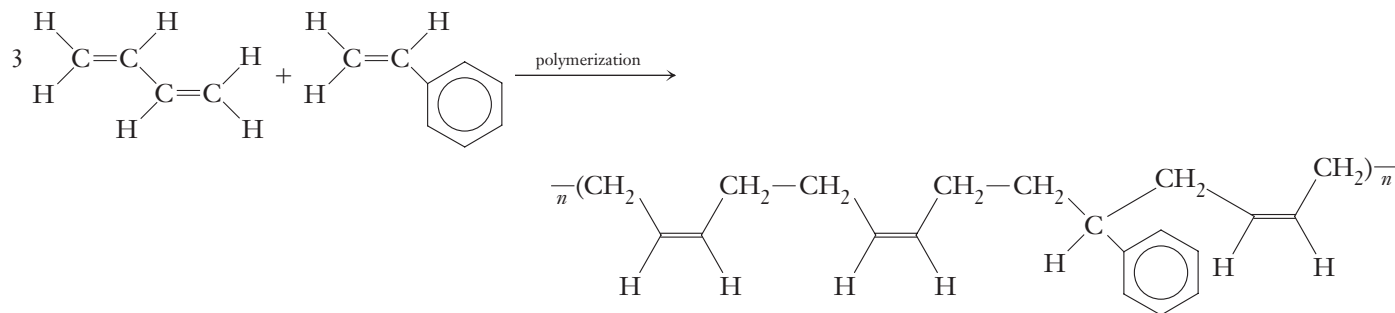
Some synthetic rubbers are superior to natural rubber in some ways. Neoprene is a synthetic elastomer (an elastic polymer) with properties quite similar to those of natural rubber. The basic structural unit is 2-chloro-1,3-butadiene, commonly called chloroprene, which differs from isoprene in having a chlorine atom rather than a methyl group at carbon 2 of the 1,3-butadiene chain.



► Numerous other polymers are elastic enough to be called by the generic name “rubber.”

Neoprene is less affected by gasoline and oil and is more elastic than natural rubber. It resists abrasion well and is not swollen or dissolved by hydrocarbons. It is widely used to make hoses for oil and gasoline, electrical insulation, and automobile and refrigerator parts.

When two different monomers are mixed and then polymerized, **copolymers** are formed. Depending on the ratio of the two monomers and the reaction conditions, the order of the units can range from quite regular (e.g., alternating) to completely random. In this way, polymers with a wide variety of properties can be produced. The most important rubber produced in the largest amount in the United States is styrene butadiene rubber (SBR), a polymer of styrene with butadiene in a 1:3 molecular ratio.



The double bonds in SBR can be cross-linked by vulcanization, as described for natural rubber. SBR is used primarily for making tires. Other copolymers are used to make car bumpers, body and chassis parts, wire insulation, sporting goods, sealants, and caulking compounds.

Some addition polymers and their uses are listed in Table 23-14.

Table 23-14 Some Important Addition Polymers

Polymer Name (some trade names)	Some Uses	Polymer Production, Tons/Year in United States	Monomer Name	Monomer Formula
polyethylene (Polythene)	electrical insulation; toys and molded objects; bags; squeeze bottles	17 million	ethylene	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$
polypropylene (Herculon, Vectra)	bottles; films; lab equipment; toys; packaging film; filament for rope, webbing, carpeting; molded auto and appliance parts	8.3 million	propylene	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{CH}_3 \end{array}$
polyvinyl chloride (PVC)	pipe, siding, gutters; floor tiles	7.1 million	vinyl chloride	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{Cl} \end{array}$
polyacrylonitrile (Orlon, Acrilan)	acrylic fibers for carpets, clothing, knitwear	95,000	acrylonitrile	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{CN} \end{array}$
polystyrene (Styrene, Styrofoam, Styron)	molded toys, dishes, kitchen equipment; insulating foam, e.g., for ice chests; rigid foam packaging	3.0 million	styrene	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{C}_6\text{H}_5 \end{array}$
poly(methyl methacrylate) (Plexiglas, Lucite)	high-quality transparent objects; water-based paints; contact lenses	507,000	methyl methacrylate	$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{C} = \text{O} \\ & & \\ & & \text{OCH}_3 \end{array}$
polybutadiene	automotive tire tread, hoses, belts; metal can coatings	610,000	1,3-butadiene	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{C} = \text{C} \\ & & / \quad \backslash \\ & & \text{H} \quad \text{H} \end{array}$
ethylene-propylene copolymer	appliance parts; auto hoses, bumpers, body and chassis parts; coated fabrics	324,000	ethylene, propylene	formulas given previously
SBR copolymer	tires	1.4 million	styrene, 1,3-butadiene	formulas given previously

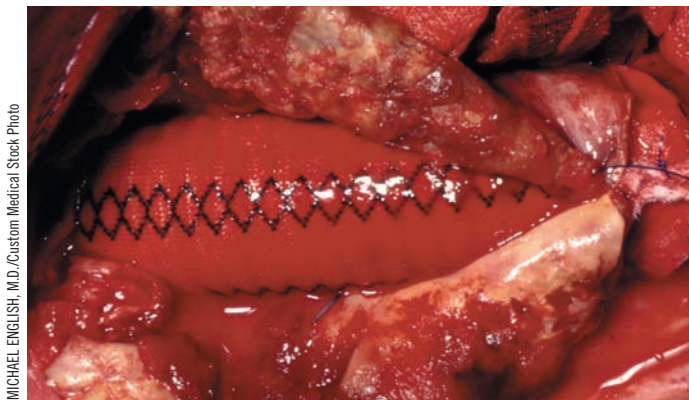
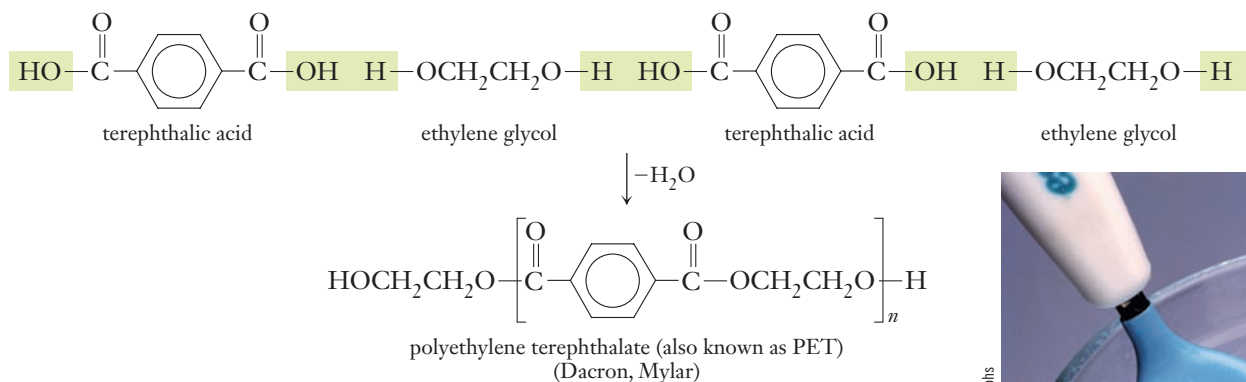
Condensation Polymerization

Some polymerization reactions are based on **condensation reactions**, in which two molecules combine by splitting out or eliminating a small molecule. For such a polymer to be formed, each monomer must have two functional groups, one on each end. A polymer formed in this way is called a **condensation polymer**. There are many useful condensation polymers, based on a wide variety of bifunctional molecules.

Polyesters (short for “polymeric esters”) are condensation polymers that are formed when *dihydric alcohols* react with *dicarboxylic acids*. An ester linkage is formed at each end of each monomer molecule to build up large molecules.

A useful polyester is prepared from terephthalic acid and ethylene glycol. More than 2 million tons of this polymer is produced annually in the United States. Dacron, the fiber produced from this polyester, accounts for approximately 50% of all synthetic fibers. It absorbs very little moisture, and its properties are nearly the same whether it is wet or dry.

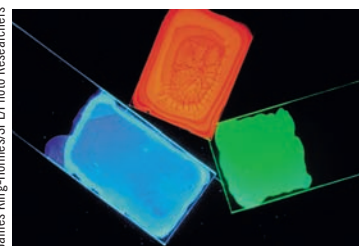
► Dihydric alcohols contain two —OH groups per molecule. They are often called glycols.



A patch made of Dacron polymer is used to close a defect in a human heart.



Richard Megna/Fundamental Photographs

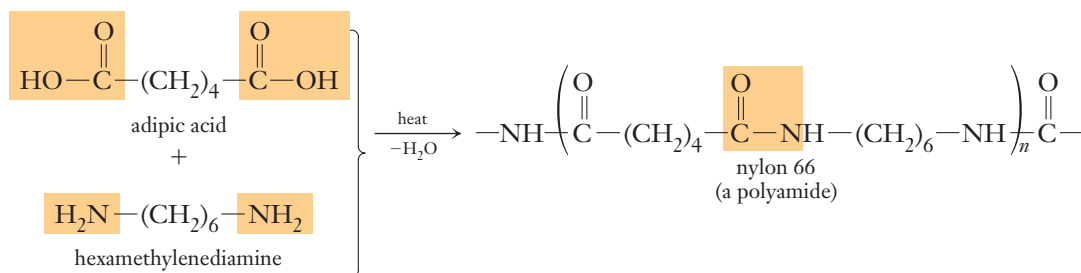


James King-Holmes/SPL/Photo Researchers

(Top) This baby feeding spoon uses a thermochromic polymer that visibly and reversibly changes color at a given temperature. The temperature at which the color change occurs can be tailored by chemical modification of the polymer. (Bottom) Light-emitting plastics, such as polyphenylene vinylene (PPV), are polymers that emit light when a voltage is applied across them. These new plastics can be made to emit light of any color and could be used in many future applications, including light-emitting diodes (LEDs) and thin-screen televisions.

Additionally, it possesses exceptional elastic recovery properties so it is used to make “permanent-press” fabrics. This polyester can also be made into films of great strength (e.g., Mylar), which can be rolled into sheets $\frac{1}{30}$ the thickness of a human hair. Such films can be magnetically coated to make audio- and videotapes.

The polymeric amides, **polyamides**, are an especially important class of condensation polymers. *Nylon* is the best known polyamide. It is prepared by heating anhydrous hexamethylenediamine with anhydrous adipic acid, a dicarboxylic acid. This substance is often called nylon 66 because the parent diamine and dicarboxylic acid each contain six carbon atoms.



Molten nylon is drawn into threads (Figure 23-22). After cooling to room temperature, these can be stretched to about four times their original length. The “cold drawing” process orients the polymer molecules so that their long axes are parallel to the fiber axis. At regular intervals there are N—H—O hydrogen bonds that *cross-link* adjacent chains to give strength to the fiber.

Petroleum is the ultimate source of both adipic acid and hexamethylenediamine. We do not mean that these compounds are present in petroleum, only that they are made from it.

► The molecular weight of the nylon polymer varies from about 10,000 to about 25,000. It melts at about 260–270°C.



Charles D. Winters

Nylon is formed at the interface where hexamethylenediamine (in the lower water layer) and adipoyl chloride (a derivative of adipic acid, in the upper hexane layer) react. The nylon can be drawn out and wound on a stirring rod. In industry, adipic acid is used in place of adipyl chloride.

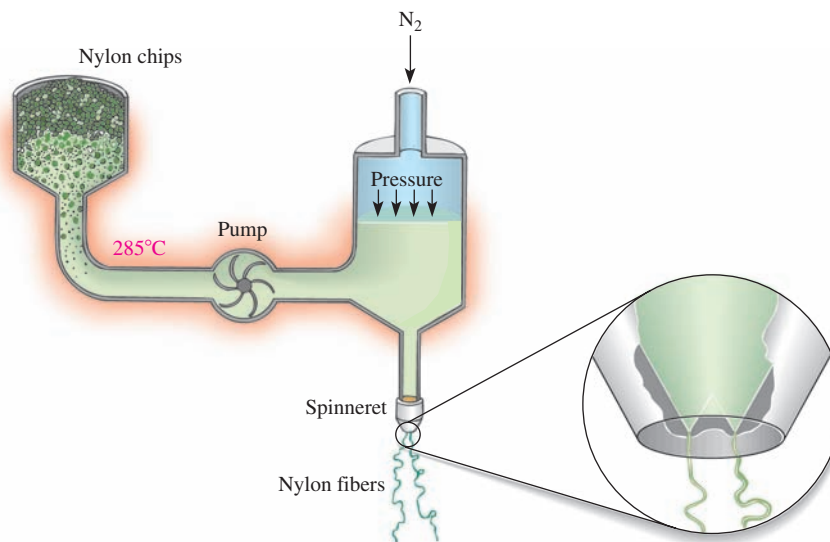
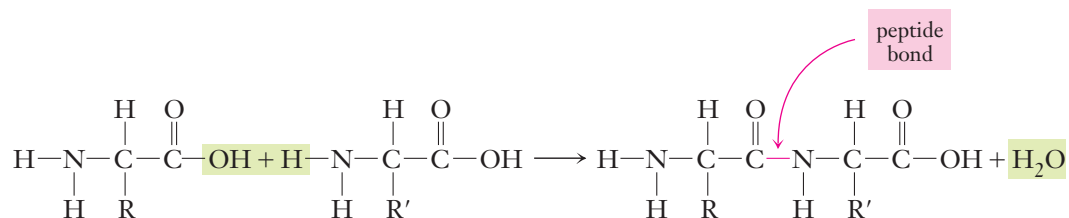


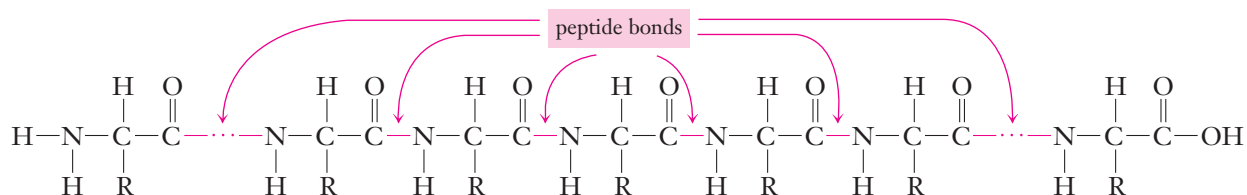
Figure 23-22 Fibers of synthetic polymers are made by extrusion of the molten material through tiny holes, called *spinnerets*. After cooling, nylon fibers are stretched to about four times their original length to orient the polymer molecules.

The same is true for many other industrial chemicals. The cost of petroleum is an important factor in our economy because so many products are derived from petroleum.

Some types of natural condensation polymers play crucial roles in living systems. **Proteins** (see Section 24-9) are polymeric chains of *L-amino acids* linked by peptide bonds. A **peptide bond** is formed by the elimination of a molecule of water between the amino group of one amino acid and the carboxylic acid group of another.



When this process is carried out repeatedly, a large molecule called a **polypeptide** is formed.



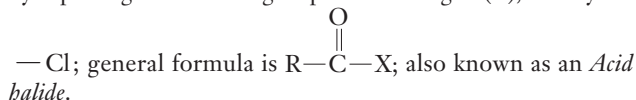
Proteins are discussed in greater detail in Section 24-9.

KEY TERMS

Acid halide See *Acyl halide*.

Acyl group The group of atoms remaining after removal of an —OH group of a carboxylic acid.

Acyl halide A compound derived from a carboxylic acid by replacing the —OH group with a halogen (X), usually

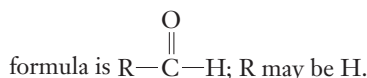


Addition polymer A polymer formed by an addition reaction.

Addition reaction A reaction in which two atoms or groups of atoms are added to a molecule, one on each side of a double or triple bond. The number of groups attached to carbon *increases*, and the molecule becomes more nearly saturated.

Alcohol A hydrocarbon derivative in which an H attached to a carbon atom not part of an aromatic ring has been replaced by an —OH group.

Aldehyde A compound in which an alkyl or aryl group and a hydrogen atom are attached to a carbonyl group; general



Aliphatic hydrocarbons Hydrocarbons that do not contain aromatic rings.

Alkanes See *Saturated hydrocarbons*.

Alkenes Unsaturated hydrocarbons that contain a carbon-carbon double bond.

Alkyl group A group of atoms derived from an alkane by the removal of one hydrogen atom.

Alkylbenzene A compound containing an alkyl group bonded to a benzene ring.

Alkynes Unsaturated hydrocarbons that contain a carbon-carbon triple bond.

Amide A compound containing the $\text{—}\overset{\text{O}}{\parallel}{\text{C}}-\text{N}<$ group.

Amine A derivative of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups.

α -Amino acid A compound containing both an amino group and a carboxylic acid group connected to a carbon atom (the α -carbon) that can have a variety of other organic groups attached. There are 22 common amino acids that are the building blocks for proteins and other biological molecules.

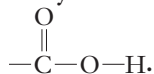
Amino group The —NR_2 group, where R can represent an H, alkyl, or aryl group.

Aromatic hydrocarbons Benzene and similar condensed ring compounds; contain delocalized rings of electrons.

Aryl group The group of atoms remaining after a hydrogen atom is removed from an aromatic system.

Carbonyl group The $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$ group.

Carboxylic acid A compound containing the carboxyl group



Condensation polymer A polymer that is formed by a condensation reaction.

Condensation reaction A reaction in which a small molecule, such as water or hydrogen chloride, is eliminated and two molecules are joined.

Conjugated double bonds Double bonds that are separated from each other by one single bond, as in $\text{C}=\text{C}-\text{C}=\text{C}$.

Constitutional isomers Compounds that contain the same numbers of the same kinds of atoms but that differ in the order in which their atoms are bonded together; also known as *structural isomers*.

Copolymer A polymer formed from two different compounds (monomers).

Cycloalkanes Cyclic saturated hydrocarbons.

Dehydration The reaction in which H— and —OH are eliminated from adjacent carbon atoms to form water and a more unsaturated bond.

Dehydrohalogenation An elimination reaction in which a hydrogen halide, HX (X = Cl, Br, I), is eliminated from a haloalkane. A $\text{C}=\text{C}$ double bond is formed.

Elimination reaction A reaction in which the number of groups attached to carbon *decreases*. The degree of unsaturation in the molecule increases.

Ester A compound of the general formula $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}'$, where R and R' may be the same or different and may be either aliphatic or aromatic. R may be H. R' cannot be H.

Ether A compound in which an oxygen atom is bonded to two alkyl or two aryl groups, or one alkyl and one aryl group.

Fat A solid triester of glycerol and (mostly) saturated fatty acids.

Fatty acid A long-chain aliphatic acid; many can be obtained from animal fats.

Functional group A group of atoms that represents a potential reaction site in an organic compound.

Geometric isomers Compounds with different arrangements of groups on the opposite sides of a bond with restricted rotation, such as a double bond; for example, *cis-trans* isomers of certain alkenes.

Glyceride A triester of glycerol.

Halogenation reaction A substitution reaction in which a hydrogen atom is replaced by a halogen atom.

Heteroatom An atom other than C or H in an organic molecule; the most common heteroatoms are O, N, S, P, and the halogens.

Heterocyclic amine An amine in which nitrogen is part of a ring.

Homologous series A series of compounds in which each member differs from the next by a specific number and kind of atoms.

Hydration reaction A reaction in which the elements of water, H and OH, add across a double or triple bond.

Hydrocarbon A compound that contains only carbon and hydrogen.

Hydrogenation The reaction in which hydrogen adds across a double or triple bond.

Isomers Different compounds that have the same molecular formula.

Ketone A compound in which a carbonyl group is bound to two alkyl or two aryl groups, or to one alkyl and one aryl group.

Monomers The small molecules that are linked to form polymers.

Oil A liquid triester of glycerol and unsaturated fatty acids.

Organic chemistry The study of carbon-containing compounds that contain C—C or C—H bonds and sometimes a few other elements such as oxygen, nitrogen, sulfur, phosphorus, and the halogens.

Peptide bond A bond formed by elimination of a molecule of water between the amino group of one amino acid and the carboxylic acid group of another.

Phenol A hydrocarbon derivative that contains an —OH group bound to an aromatic ring.

Pi (π) bond A chemical bond formed by the side-to-side overlap of atomic orbitals.

Polyamide A polymeric amide.

Polyene A compound that contains more than one double bond per molecule.

Polyester A polymeric ester.

Polymerization The combination of many small molecules (monomers) to form large molecules (polymers).

Polymers Large molecules formed by the combination of many small molecules (monomers).

Polyol An alcohol that contains more than one —OH group; a polyol with two —OH groups is called a glycol.

Polypeptide A polymer composed of amino acids linked by peptide bonds.

Primary alcohol An alcohol with a CH_3 or CH_2 —R group bonded to the carbon bearing the —OH group.

Primary amine An amine in which one H atom of ammonia has been replaced by an organic group.

Protein A naturally occurring polymeric chain of L-amino acids linked together by peptide bonds.

Saturated hydrocarbons Hydrocarbons that contain only single bonds; also known as *alkanes* or *paraffin hydrocarbons*.

Secondary alcohol An alcohol with two R groups bonded to the carbon bearing the —OH group.

Secondary amine An amine in which two H atoms of ammonia have been replaced by organic groups.

Sigma (σ) bond A chemical bond formed by the end-to-end overlap of atomic orbitals.

Structural isomers See *Constitutional isomers*.

Substitution reaction A reaction in which an atom or a group of atoms attached to a carbon atom is replaced by another atom or group of atoms. No change occurs in the degree of saturation at the reactive carbon.

Tertiary alcohol An alcohol with three R groups bonded to the carbon bearing the —OH group.

Tertiary amine An amine in which three H atoms of ammonia have been replaced by organic groups.

Unsaturated hydrocarbons Hydrocarbons that contain double or triple carbon-carbon bonds.

Vulcanization The process in which sulfur is added to rubber and heated to 140°C to cross-link the linear rubber polymer into a three-dimensional polymer.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Basic Ideas

1. ● (a) Give a brief definition of organic chemistry. (b) Can life, as currently known, exist without organic compounds? (c) The Vital Force Theory was proposed by Berzelius in 1809 and stated that organic compounds could only be formed in living cells and that it was impossible to prepare them in laboratories. Discuss why this theory is true or false.



Some organic products

2. ● How is it possible that there are so many different compounds that are hydrocarbons, when each contains the same two elements?
3. ● (a) Why do many organic compounds have low melting and boiling points? (b) Some organic compounds, like table sugar, do not have a boiling point. Suggest a reason why.
4. ● (a) What are the principal sources of organic compounds? (b) Some chemists argue that the ultimate source of all naturally occurring organic compounds is carbon dioxide. Could this be possible? *Hint:* Think about the origins of coal, natural gas, and petroleum.
5. List 10 “everyday” uses of organic compounds. Choose examples from at least five different classes of compounds.

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

31. Each of the hydrocarbon families has members that are cyclic hydrocarbons. (a) What is a cyclic hydrocarbon? (b) Write the structural formula of one example of each of the following: (i) cycloalkene; (ii) cycloalkane; and (iii) cycloalkyne.

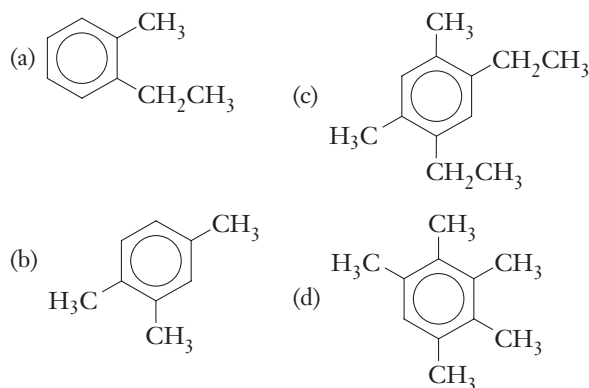
Aromatic Hydrocarbons

32. (a) What distinguishes an aromatic compound from other cyclic compounds? (b) What is the principal source of aromatic hydrocarbons?



Some mixtures of aromatic compounds

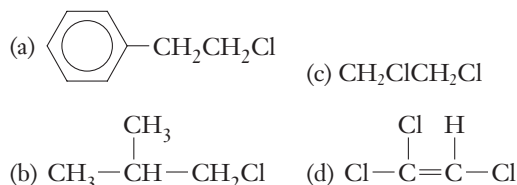
33. (a) The structure for benzene is sometimes drawn as a hexagon enclosing a circle. What is the meaning of the circle? (b) Write the structural formulas of the three most common aromatic hydrocarbons.
34. (a) What is a phenyl group? (b) How many isomeric monophenylnaphthalenes are possible?
35. There are only three isomeric trimethylbenzenes. Write their structural formulas, and name them.
36. (a) How many isomeric dibromobenzenes are possible? (b) What names are used to designate these isomers?
37. Write the structural formulas for the following compounds: (a) *o*-chlorofluorobenzene; (b) ethylbenzene; (c) 1,3,5-tribromobenzene; (d) 1,3-diphenylbutane; (e) *p*-chlorotoluene.
38. Write the IUPAC names for the following compounds.



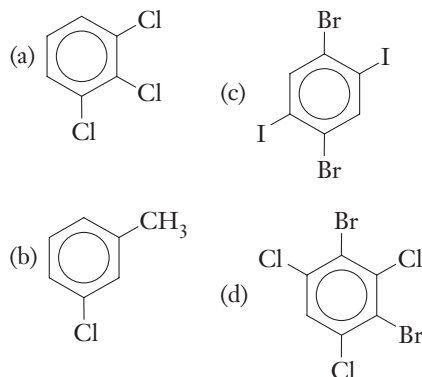
Alkyl and Aryl Halides

39. (a) Write the general representation for the formula of an alkyl bromide. (b) How does this differ from the representation for the formula of an aryl bromide?

40. Write the IUPAC names for the following halides.



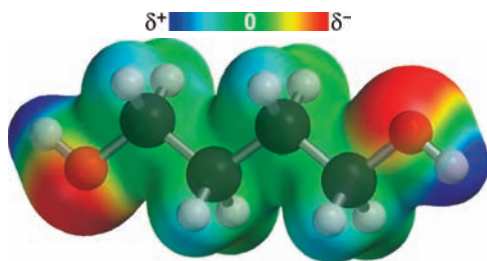
41. Write the structural formulas for the following: (a) 1,2-dichloropentane; (b) 4-bromo-1-butene; (c) 1,2-dichloro-2-fluoropropane; (d) *p*-dichlorobenzene.
42. Name the following.



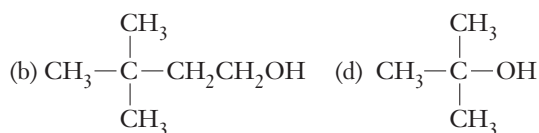
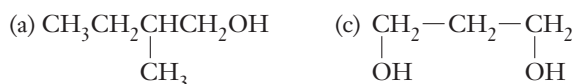
43. The compound 1,2-dibromo-3-chloropropane (DBCP) was used as a pesticide in the 1970s. Recently, agricultural workers have claimed that exposure to DBCP made them sterile. Write the structural formula for this compound.

Alcohols and Phenols

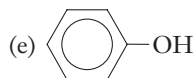
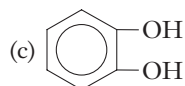
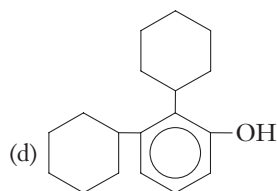
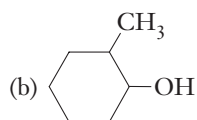
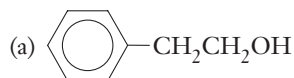
44. (a) What are alcohols and phenols? (b) How do they differ? (c) Why can alcohols and phenols be viewed as derivatives of hydrocarbons? as derivatives of water?
45. (a) Distinguish among primary, secondary, and tertiary alcohols. (b) Write names and formulas for three alcohols of each type.
46. Write structural formulas for and the IUPAC names of the eight (saturated) alcohols that contain five carbon atoms and one —OH group per molecule. Which ones may be classified as primary alcohols? Secondary alcohols? Tertiary alcohols?
47. (a) What are glycols? (b) Write the structural formula of three examples. (c) Why are glycols more soluble in water than monohydric alcohols that contain the same number of carbon atoms?
48. Refer to Table 23-8 and explain the trends in boiling points and solubilities of alcohols in water.
49. Why are methyl alcohol and ethyl alcohol called wood alcohol and grain alcohol, respectively?
50. Why are most phenols only slightly soluble in water?
51. Write the structural formula for each of the following compounds: (a) 2-butanol; (b) cyclohexanol; (c) 1,4-butanediol. (d) Which of these compounds is (are) represented by the following model?



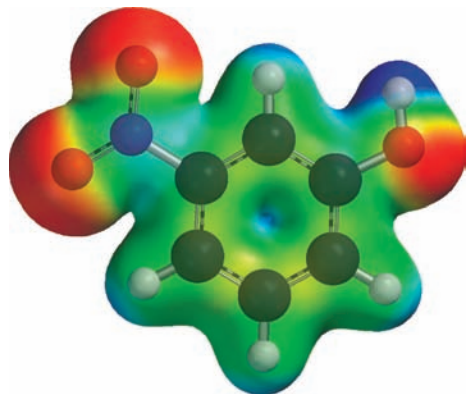
52. Give the IUPAC name for each of the following compounds.



53. Which of the following compounds are phenols? Give the IUPAC name for each compound.

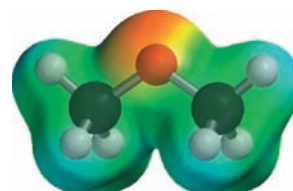


54. Write the structural formulas for the following: (a) *p*-chlorophenol; (b) 3-nitrophenol (the nitro group is $-\text{NO}_2$); (c) *m*-nitrophenol. (d) Which of these compounds is (are) represented by the following model?

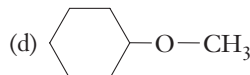
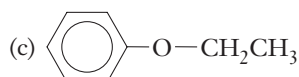
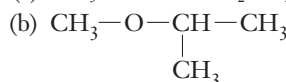
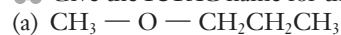


Ethers

55. Distinguish among aliphatic ethers, aromatic ethers, and mixed ethers. Give an example of each.
56. Briefly describe the bonding around the oxygen atom in dimethyl ether. What intermolecular forces are found in this ether?
57. What determines whether an ether is classified as aliphatic, aromatic, or mixed? Give an example of each.
58. Write the structural formulas for the following: (a) methoxymethane; (b) 2-methoxypropane; (c) 1,2-diethoxybutane; (d) ethoxybenzene; (e) methoxycyclobutane. (f) Which of these compounds is (are) represented by the following model?

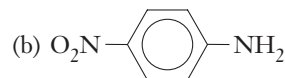
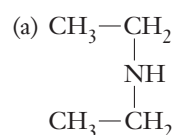


59. Give the IUPAC name for the following ethers.

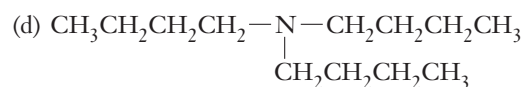
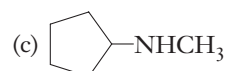


Amines

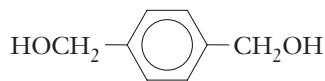
60. (a) What are amines? (b) Why are amines described as derivatives of ammonia?
61. Write the general representation for the formula for a compound that is (a) a primary amine, (b) a secondary amine, (c) a tertiary amine. (d) Is $(\text{CH}_3)_2\text{CHNH}_2$ a secondary amine? Give a reason for your answer.
62. Name the following amines.



(The $-\text{NO}_2$ substituent is called "nitro-.")



84. ● Most reactions of the alkanes that do not disrupt the carbon skeleton are substitution reactions, whereas the alkenes are characterized by addition to the double bond. What does this statement mean?
85. ● How can bromination be used to distinguish between alkenes and alkanes?
86. ● Write equations for two reactions in which alkenes undergo addition reactions with halogens. Give the IUPAC names for all compounds.
87. ● When a substitution reaction occurs, there is no change in saturation. Explain.
88. ● (a) What is hydrogenation? (b) Why is it important? (c) Write equations for two reactions that involve hydrogenation of alkenes. (d) Give the IUPAC names for all compounds in part (c).
89. ● Describe two qualitative tests that can be used to distinguish between alkenes and alkanes. (b) Cite some specific examples. (c) What difference in reactivity is the basis for the qualitative distinction between alkanes and alkenes?
90. ● (a) Why are alkynes more reactive than alkenes? (b) What is the most common kind of reaction that alkynes undergo? (c) Write equations for three such reactions. (d) Give the IUPAC names for all compounds in part (c).
91. ● (a) What is the most common kind of reaction that the benzene ring undergoes? (b) Write equations for the reaction of benzene with chlorine in the presence of an iron catalyst and for the analogous reaction with bromine.
92. ● Write equations to illustrate both aromatic and aliphatic substitution reactions of toluene using (a) chlorine, (b) bromine, and (c) nitric acid.
93. ● Classify each reaction as substitution, addition, or elimination.
 (a) $\text{CH}_3\text{CH}_2\text{Br} + \text{CN}^- \rightarrow \text{CH}_3\text{CH}_2\text{CN} + \text{Br}^-$
 (b) $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{Br} + \text{Zn} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{ZnBr}_2$
 (c) $\text{C}_6\text{H}_6 + \text{HNO}_3 \longrightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$
94. ● Describe a simple test to distinguish between the two isomers 2-pentene and cyclopentane.
96. ● (a) What is polymerization? (b) Write equations for three polymerization reactions.
97. ● (a) Give an example of a condensation reaction. (b) What is the essential feature of monomers used in condensation polymerizations?
98. ● (a) What is a copolymer? (b) What is a condensation polymer? (c) Name three polymers that are addition polymers.
99. ● Polyvinyl alcohol has a relatively high melting point, 258°C. How would you explain this characteristic? A segment of the polymer is
- $$\cdots \text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2\underset{\text{OH}}{\text{CH}} \cdots$$
100. ● What changes could be made in the structures of polymer molecules that would increase the rigidity of a polymer and raise its melting point?
101. ● Methyl vinyl ketone, $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}=\text{CH}_2$, can be polymerized by addition polymerization. The addition reaction involves only the $\text{C}=\text{C}$ bond. Write the structural formula of a four-unit segment of this polymer.
102. ● (a) What is rubber? (b) What is vulcanization? (c) What is the purpose of vulcanizing rubber? (d) What are fillers and reinforcing agents? (e) What is their purpose?
103. ● (a) What is an elastomer? (b) Cite a specific example. (c) What are some of the advantages of neoprene compared with natural rubber?
104. ● (a) What are polyamides? (b) In what kind of reaction are polyamides formed?
105. ● (a) What are polyesters? (b) What is Dacron? (c) How is Dacron prepared? (d) What is Mylar? (e) Is it reasonable to assume that a polyester can be made from propylene glycol and terephthalic acid? If so, sketch its structure.
106. ● Suppose the following glycol is used with terephthalic acid to form a polyester. Write the structure of the polymer, showing two repeating units.



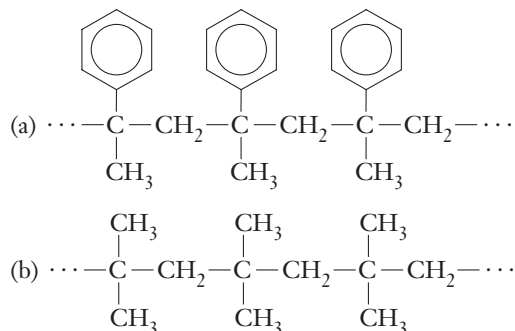
Polymers

95. ● (a) What is a polymer? (b) What is the term for the smaller molecule that serves as the repeating unit making up a polymer? (c) What are typical molecular weights of polymers? (d) Name three polymers commonly found in the classroom and give their use or function.



Common products made from polymers

107. ● Write the structural formula of the monomer used in preparation of each of the following polymers.



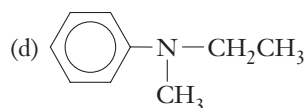
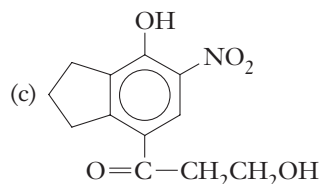
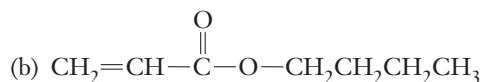
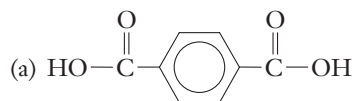
108. ● Is it possible to produce a copolymer by addition polymerization? If so, give an example. If not, explain why not.
109. ● (a) What is nylon? (b) How is it prepared?
110. ● Common nylon is called nylon 66. (a) What does this mean? (b) Write formulas for two other possible nylons.

Mixed Exercises

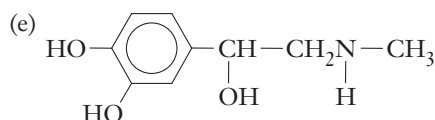
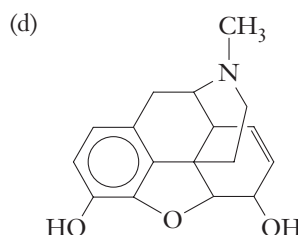
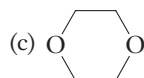
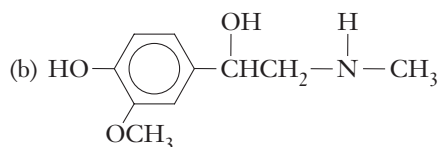
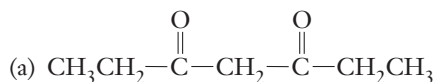
111. ● Write structural formulas for the following alkanes.
- 2,2,4-trimethylpentane
 - 2,2-dimethylpropane
 - 4-isopropyloctane
 - 2,3,4-trimethylheptane
112. ● Write the formula for
- an alkyne with 16 hydrogen atoms.
 - an alkene with 44 hydrogen atoms.
 - an alkane with 10 carbon atoms.
113. ● ▲ Identify the class of organic compounds (ester, ether, ketone, etc.) to which each of the following belongs.
- -
 -
 -

114. ● ▲ Identify the class of organic compounds (ester, ether, ketone, etc.) to which each of the following belongs.
- -
 -
 -

115. ● ▲ Identify and name the functional groups in each of the following.

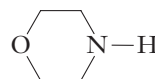


116. ● Identify and name the functional groups in the following.

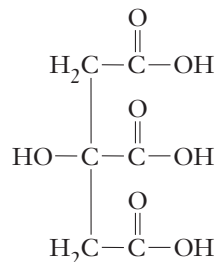


117. ● Identify and name the functional groups in each of the following.

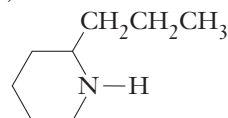
- (a) morpholine



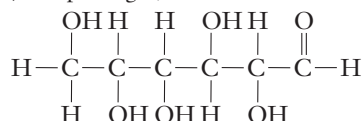
- (b) citric acid



- (c) coniine (from the hemlock plant; the poison that Socrates drank)

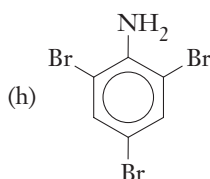
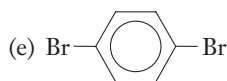
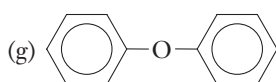
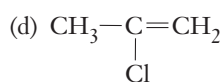
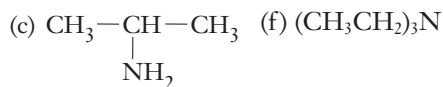
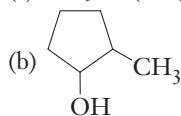


- (d) glucose (a simple sugar, also known as dextrose)

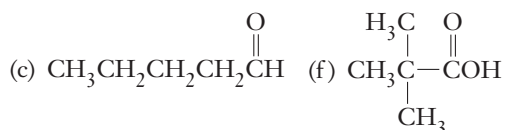
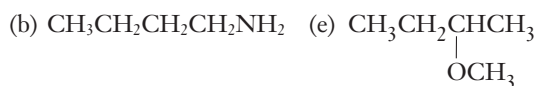
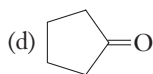
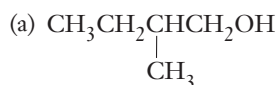


OCC1C(O)C(=O)C(O)O1

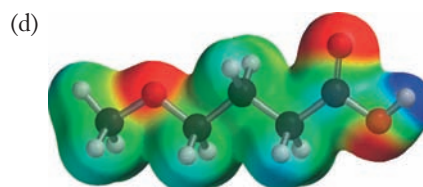
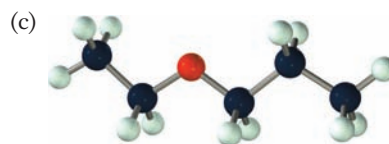
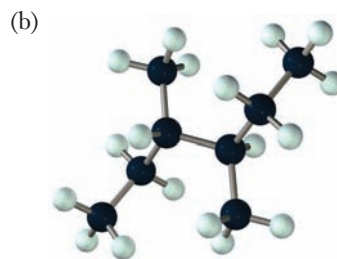
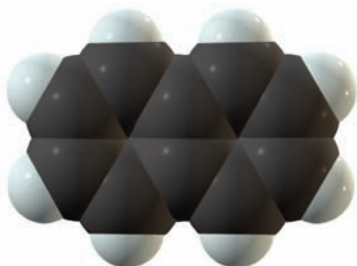
(a) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$



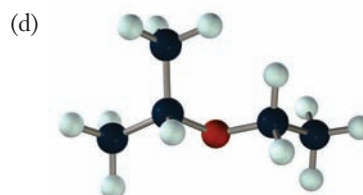
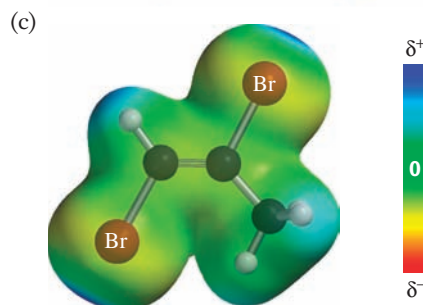
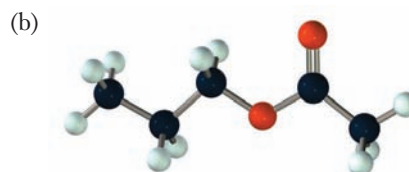
120. Give the IUPAC names for the following compounds.



(a)



(a)



Conceptual Exercises

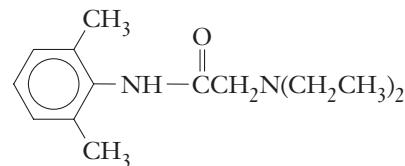
123. Explain why the C_6 ring in cyclohexane is not planar.
124. Can an aromatic compound also be a saturated compound?
125. Is it possible for a cycloalkane to be both flat and without bond angle strain?
126. Which compound has the smaller amount of strain when forced to have all its carbons in a plane (flat), cyclohexane or cyclopentane? Explain.
127. Describe the hybrid orbitals utilized by each carbon atom in cyclohexene.
128. Describe the hybrid orbitals utilized by each carbon atom in 1,3-cyclohexadiene.
129. Which classes of organic compounds contain a carbonyl functional group?
130. Which classes of organic compounds must contain an aromatic group?
131. Hydrocarbons contain atoms of which elements? What classes of organic compounds contain only these elements and oxygen? What classes of organic compounds contain only nitrogen and the elements found in hydrocarbons?
132. How are single, double, and triple carbon-carbon bonds different from each other?
133. How is the classification of alcohols into primary, secondary, or tertiary different from the classification of amines into primary, secondary, or tertiary (other than that alcohols contain oxygen and amines contain nitrogen)?
134. What functional groups and molecular characteristics tend to make organic compounds soluble in water?
135. Name six classes of organic compounds that include the group $>C=O$ in some form.
136. Predict the physical and chemical properties of *cis*-5-pentacosene, $C_{25}H_{50}$ or $CH_3(CH_2)_3CH=CH(CH_2)_{18}CH_3$, which is used by fruit flies in their chemical communication system.

Building Your Knowledge

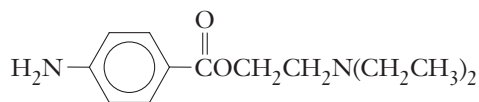
137. (a) How do the melting points and boiling points of the alkanes vary with molecular weight? (b) Do you expect them to vary in this order? (c) Why or why not? Use intermolecular forces to explain your answer.
138. Methyl ethyl ketone (MEK) is a common industrial solvent. Its IUPAC name is butanone. Write its Lewis formula and show how its common name, MEK, is derived.

139. (a) What are resonance structures? (b) Draw resonance structures for benzene. (c) What do we mean when we say that the electrons associated with the pi bonds in benzene are delocalized over the entire ring?

140. Lidocaine has replaced Novocain (procaine) as the favored anesthetic in dentistry. What functional group do the two compounds have in common?



Lidocaine



Novocain

141. PHB stands for poly(hydroxybutanoate). (a) Write the structural formula of 4-hydroxybutanoic acid. (b) Write the structural formula of an ester that can be formed from two molecules of 4-hydroxybutanoic acid. How is it formed? Would the ester be very soluble in water? Give a reason for your answer. (c) Write the repeating unit in the polymeric form of the polyester, hydroxybutanoate.

Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

142. Use an internet search engine to locate information on petroleum cracking. Describe thermal cracking. Describe catalytic cracking. In the petroleum industry, which is used more today?
143. Use an internet search engine to locate information on cyclohexane. List four industrial uses of cyclohexane. What industry consumes more than half of all the cyclohexane produced?
144. Use a reference book or an internet search engine to locate information on naphtha. Describe naphtha.
145. Use an internet search engine to locate information on oil wells. When and where was the first producing oil well? Were petroleum products used before the first producing oil well was developed?

Organic Chemistry II: Shapes, Selected Reactions, and Biopolymers

24



Capsaicin, the substance responsible for the “hot” in peppers, has phenol, ester, and amide functional groups. In addition to acting as an inflammatory agent, it can act as a pain reliever, presumably by blocking nerve endings involved in the transmission of pain.

David Cavagnaro/Visuals Limited

OUTLINE

Shapes of Organic Molecules

- 24-1** Constitutional Isomers
- 24-2** Stereoisomers
- 24-3** Conformations

Selected Reactions

- 24-4** Reactions of Brønsted–Lowry Acids and Bases
- 24-5** Oxidation–Reduction Reactions
- 24-6** Formation of Carboxylic Acid Derivatives
- 24-7** Hydrolysis of Esters

Biopolymers

- 24-8** Carbohydrates
- 24-9** Polypeptides and Proteins
- 24-10** Nucleic Acids

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Describe the differences between constitutional isomers and stereoisomers
- ▶ Distinguish between isomers and conformations
- ▶ Describe some common organic acids and bases and their relative strengths
- ▶ Recognize some reactions that involve oxidation and reduction of organic compounds
- ▶ Recognize reactions that form carboxylic acid derivatives
- ▶ Recognize reactions in which esters and amides are formed
- ▶ Write equations in which carbonyl groups are used to produce other functional groups
- ▶ Write equations showing the hydrolysis of esters (saponification)
- ▶ Describe the structure of carbohydrates
- ▶ Describe the structure of proteins
- ▶ Describe the structure of nucleic acids

Shapes of Organic Molecules

As we learned in Chapter 23, the chemical and physical properties of a substance depend on the arrangements, as well as the identities, of its atoms.

Isomers are substances that have the same number and kind of atoms—the same *molecular formula*—but with different structural formulas. *Because their structures are different, isomers are different substances and have different properties.*

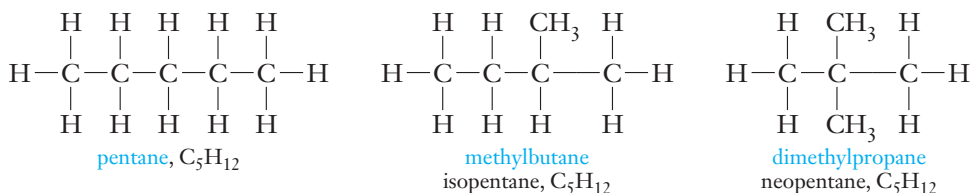
Isomers can be broadly divided into two major classes: constitutional isomers and stereoisomers. In Chapter 23 we learned about some isomeric organic compounds. In this chapter, we will take a more systematic look at some three-dimensional aspects of organic structures—a subject known as **stereochemistry** (“spatial chemistry”).

24-1 Constitutional Isomers

Constitutional (or **structural**) **isomers** differ in the *order* in which their atoms are bonded together.

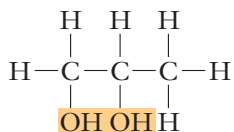
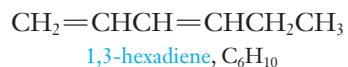
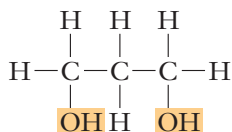
In our studies of hydrocarbons in Sections 23-1 through 23-7, we saw some examples of constitutional isomerism in hydrocarbons. Recall, for instance, that there are three isomers of C_5H_{12} .

▶ Names in blue print are systematic (IUPAC) names. Names in black print are common or trivial names.

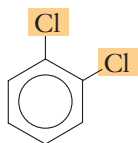
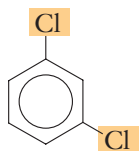
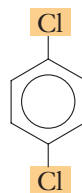


These three isomers differ in the lengths of their base chains but not in the functional groups present (i.e., only alkyl groups are present in this case). As a result, they differ somewhat in their melting and boiling points but differ only very slightly in the reactions they undergo.

In one kind of constitutional isomerism, known as *positional isomers*, the compounds have the same *number* and *kind* of functional groups on the *same base chain* or the *same ring*, but in different positions. Isomers that vary only in the location of groups of atoms usually have very similar chemical and physical properties, differing mainly in physical properties such as melting and boiling points. The following groups of isomers are examples in which the type of functional group does not change.

1,2-propanediol, $\text{C}_3\text{H}_8\text{O}_2$ 1,3-propanediol, $\text{C}_3\text{H}_8\text{O}_2$

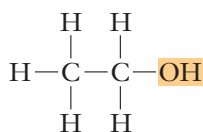
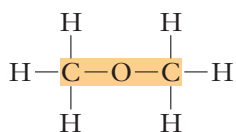
► These are *positional isomers*.

*o*-dichlorobenzene, $\text{C}_6\text{H}_4\text{Cl}_2$ *m*-dichlorobenzene, $\text{C}_6\text{H}_4\text{Cl}_2$ *p*-dichlorobenzene, $\text{C}_6\text{H}_4\text{Cl}_2$

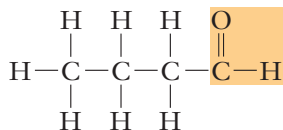
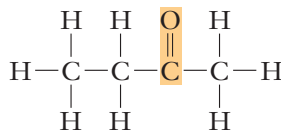
Sometimes the different order of arrangements of atoms results in different functional groups. Some examples of this type of constitutional isomerism follow.

► These may also be referred to as *functional group isomers*.

An alcohol and an ether:

ethanol, $\text{C}_2\text{H}_6\text{O}$ methoxymethane, $\text{C}_2\text{H}_6\text{O}$
(dimethyl ether)

An aldehyde and a ketone:

butanal, $\text{C}_4\text{H}_8\text{O}$
(butyraldehyde)butanone, $\text{C}_4\text{H}_8\text{O}$
(methyl ethyl ketone)

24-2 Stereoisomers

In **stereoisomers** the atoms are linked together in the *same* atom-to-atom order, but their *arrangements in space* are different.

There are two types of stereoisomers: geometric and optical.

Geometric Isomers

Geometric isomers (or *cis-trans* isomers) differ only in the spatial orientation of groups about a plane or direction. Two geometric isomers have the same molecular formula, the same functional groups, the same base chain or ring, and the same order of attachment of atoms; they differ in orientation either (1) around a double bond or (2) across the ring in a cyclic compound.

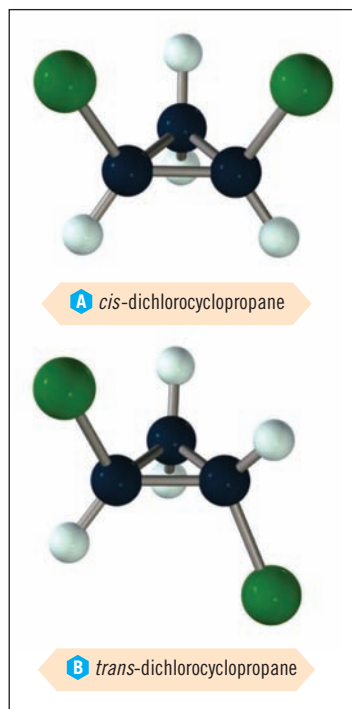


Figure 24-1

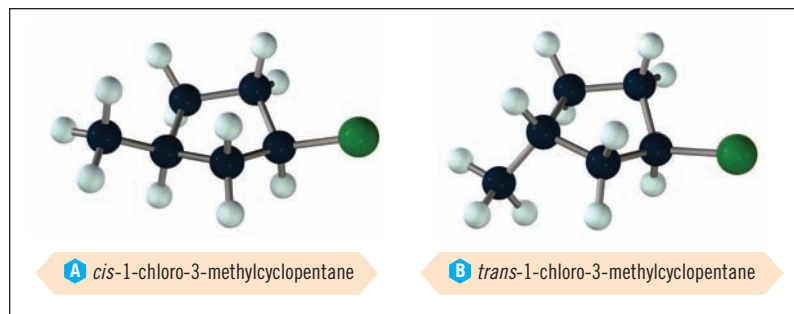


Figure 24-2

If the larger groups are on opposite sides of the ring or the double bond, the designation *trans* appears in the name; if they are on the same side, the designation is *cis*. We learned in Section 23-3 about the geometric isomerism associated with the double bond in alkenes such as the 1,2-dichloroethenes (see Figure 23-9). Similarly, two or more substituents can be either on the same side or on opposite sides of the ring, as shown in Figures 24-1 and 24-2. This kind of isomerism is possible when substituents have replaced an H from a $\text{—CH}_2\text{—}$ unit in a ring. Because substituents on an aromatic ring are bonded in the plane of the ring, such substitutions do not lead to geometric isomerism.

Optical Isomers

Many objects are mirror images of each other and cannot be superimposed. Your two hands are a familiar example of this; each hand is a nonsuperimposable mirror image of the other (Figure 24-3). “Superimposable” means that if one object is placed over the other, the positions of all parts will match.

An object that is *not* superimposable with its mirror image is said to be **chiral** (from the Greek word *cheir*, meaning “hand”); an object that *is* superimposable with its mirror image is said to be **achiral**. Examples of familiar objects that are chiral are a screw, a propeller, a foot, an ear, and a spiral staircase; examples of common objects that are achiral are a plain cup with no decoration, a pair of eyeglasses, and a sock.

Optical isomers that are nonsuperimposable mirror images of each other (chiral) are called **enantiomers** of one another. Enantiomers can exist in two forms that bear the same relationship to each other as do left and right hands.

As an example of this, consider first the two models of bromochloromethane, CH_2BrCl , shown in Figure 24-4a. They are mirror images of each other, and they can be superimposed. Thus, this molecule is *achiral* and is not capable of optical isomerism. Now consider bromochloriodomethane, CHBrClI (see Figure 24-4b, c, and d). This molecule is not superimposable with its mirror image, so it is *chiral*, and the two forms are said to be enantiomers of each other. Any compound that contains four different atoms or groups bonded to the same carbon atom is chiral; that is, it exhibits optical isomerism. Such a carbon is said to be *asymmetric* (meaning “without symmetry”). Most simple chiral molecules contain at least one asymmetric carbon atom, although there are other ways in which molecular chirality can occur.

Stereoisomers have the same type and number of atoms, connected in the same order, but arranged differently in space. Optical isomers (enantiomers) and geometric isomers are subgroups of stereoisomers. They differ, however, in that geometric isomers have *different* physical and chemical properties, whereas optical isomers have physical properties that are identical (e.g., melting point, boiling point, and density). Optical isomers also undergo the same chemical reactions, except when they interact with other chiral compounds. Consequently, their properties in biological systems may be very different. They also often exhibit different solubilities in solvents that are composed of chiral molecules.

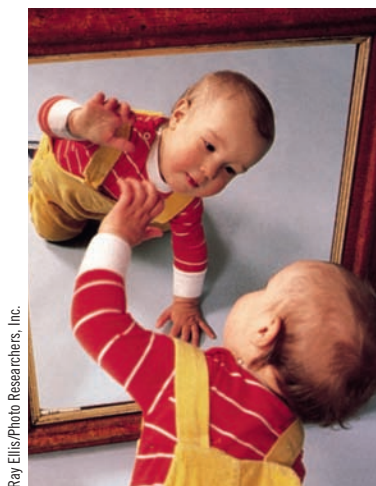


Figure 24-3 Mirror images. Place your left hand in front of a mirror; you will observe that it looks like your real right hand. We say that the two hands are mirror images of each other; each hand is in every way the “reverse” of the other. Now try placing one hand directly over the other; they are not identical. Hence, they are nonsuperimposable mirror images. Each hand is a *chiral* object. We speak of a screw or a propeller as being “right-handed” or “left-handed.”

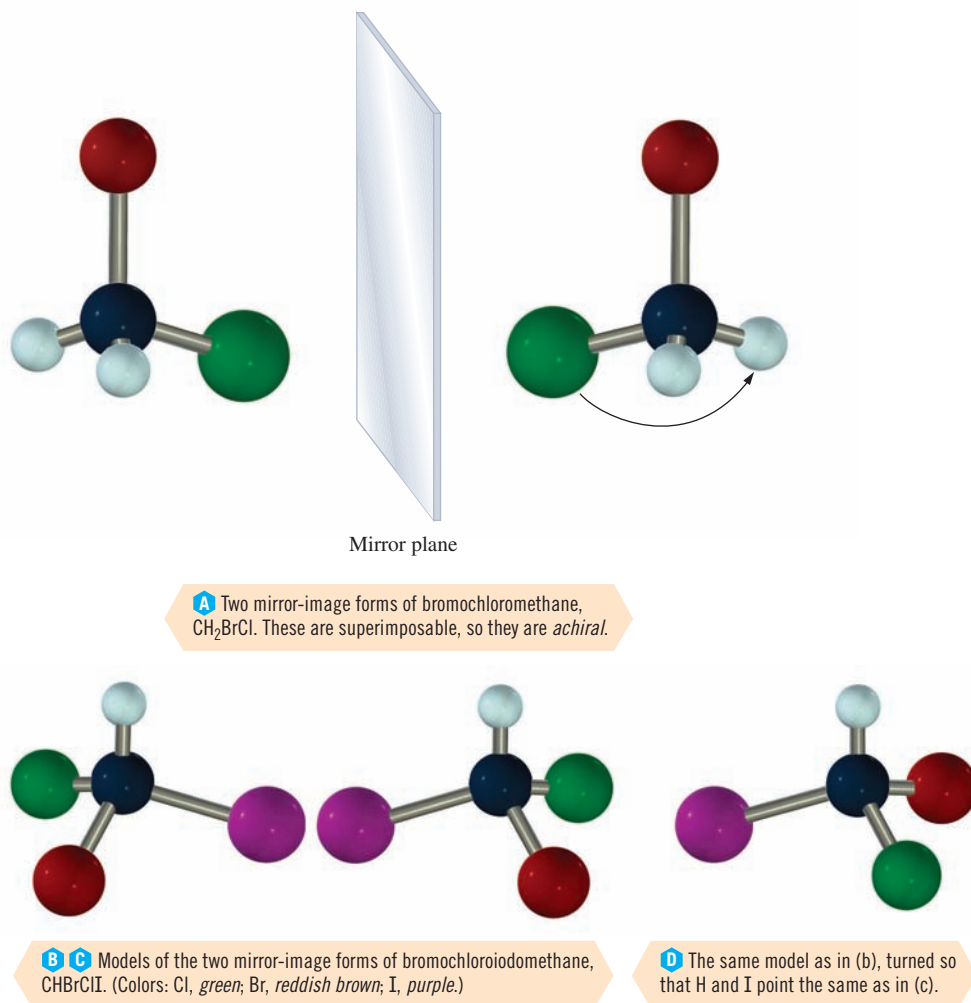


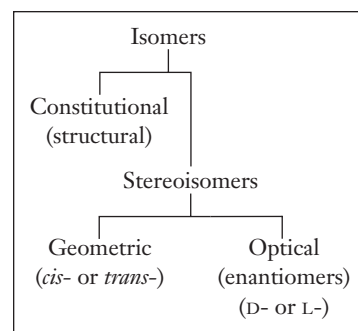
Figure 24-4 (a) Models of two mirror-image forms of bromochloromethane, CH_2BrCl . The two models are the same (superimposable). They are *achiral*, and any solution of CH_2BrCl does *not* exhibit optical isomerism.

Models (b) and (c) show the two mirror-image forms of bromochloroiodomethane, CHBrClI . The two models (b) and (c) cannot be superimposed on each other no matter how we rotate them. They are *chiral*, so they represent *optical isomers*.

Model (d) is the same as (b), but turned so that the H and I atoms point the same as in (c). However, the Br and Cl atoms are not in the same directions in (d) and (c). Now models (d) and (b) represent the *same compound*.

Optical isomers also differ from one another in one important physical property: They interact with polarized light in different ways. Separate equimolar solutions of two optical isomers rotate plane-polarized light by equal amounts but in opposite directions (Figure 24-5a). One solution is called **dextrorotatory** (rotates light to the *right*) and the other is **levorotatory** (rotates to the *left*). One of the optical isomers can be designated as the D-isomer (*dextro*), and its nonsuperimposable mirror image is designated as the L-isomer (*levo*).

The phenomenon in which plane-polarized light is rotated by a sample of either isomer is called **optical activity**. It can be measured with a *polarimeter* (see Figure 24-5b) or with more sophisticated instruments. A single solution containing equal amounts of the two opposite isomers is a **racemic mixture**. The equal and opposite effects of the two isomers in such a solution exactly cancel, so this solution does not rotate plane-polarized light. To exhibit optical activity, the *dextro* and *levo* isomers must be separated from one another. This is done by one of a number of chemical or physical processes broadly called *optical resolution*.



Unless otherwise noted, all content on this page is © Cengage Learning.

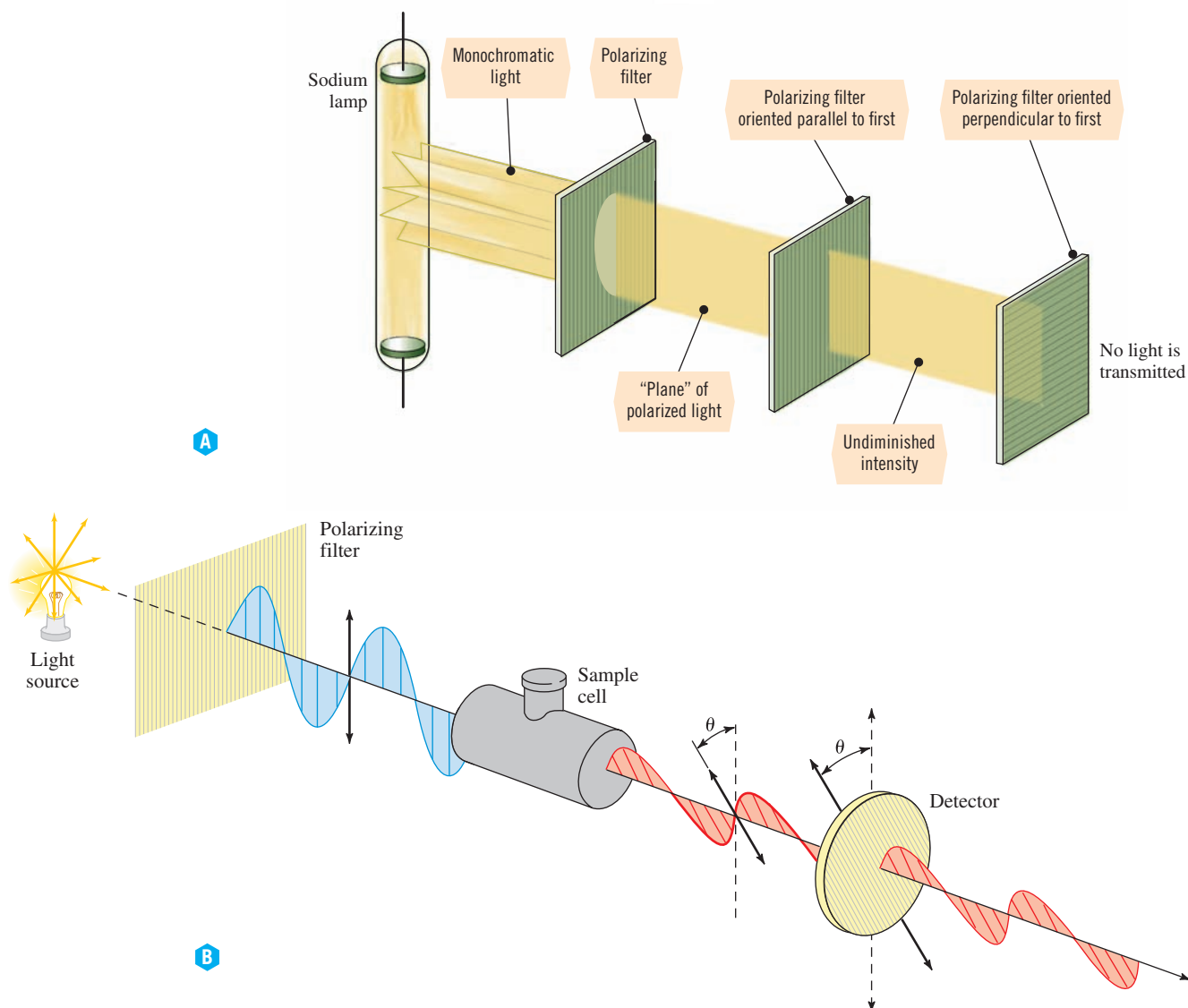
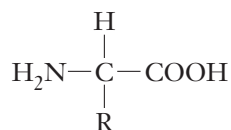


Figure 24-5 (a) Light from a lamp or from the sun consists of electromagnetic waves that vibrate in all directions perpendicular to the direction of travel. Polarizing filters absorb all waves except those that vibrate in a single plane. All of this plane-polarized light passed by the first polarizing filter is also passed by the second, parallel filter. The third polarizing filter, with a plane of polarization at right angles to the first, absorbs the polarized light completely. (b) The principles of a **polarimeter**. The plane of polarization of plane-polarized light is rotated through an angle (θ) as it passes through an optically active medium. Species that rotate the plane to the right (clockwise as shown here) are dextrorotatory, and those that rotate it to the left are levorotatory.

One very important way in which optical isomers differ chemically from one another is in their biological activities. α -Amino acids have the general structure



where R represents any of a number of common substituents. The central carbon atom has four atoms or groups bonded to it. In α -amino acids the four groups are all different, so

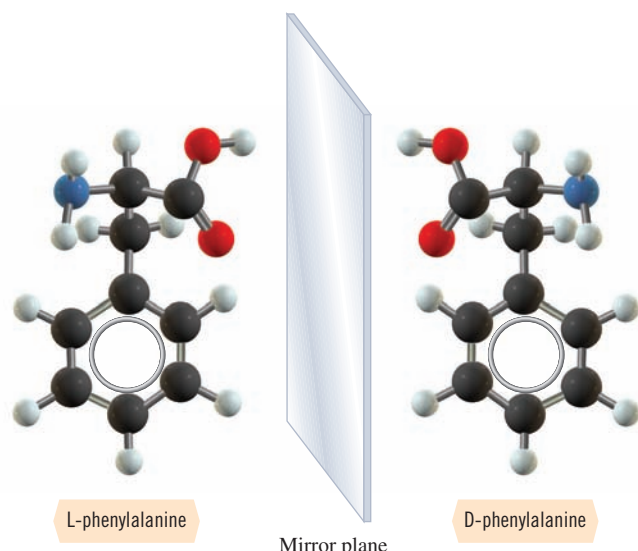


Figure 24-6 Models of the two optical isomers of phenylalanine. The naturally occurring phenylalanine in all living systems is the form shown on the left.

each amino acid can exist as two optical isomers. The exception is glycine, in which $R = H$. Figure 24-6 shows this mirror-image relationship for optical isomers of phenylalanine, in which $R = -CH_2C_6H_5$. All naturally occurring phenylalanine in living systems is the L-form. In fact, only one isomer of each of the various optically active amino acids is found in proteins.

24-3 Conformations

The **conformations** of a compound differ from one another in the *extent of rotation about one or more single bonds*. The $C-C$ single bond length, $1.54 \text{ \AA}$, is relatively independent of the structure of the rest of the molecule.

Rotation about a single $C-C$ bond is possible; in most compounds at room temperature it occurs very rapidly. In drawings and models, such as those in Figure 24-7, it might at first appear that rotation about a single bond would be totally unrestricted. The electrons of the groups attached to the carbon atoms do repel one another somewhat, however. At room temperature, ethane molecules possess sufficient energy to cause rapid rotation about the single carbon-carbon bond from one conformation to another. The staggered conformation of ethane is slightly more stable (of lower energy) than the eclipsed conformation (see Figure 24-7); in the eclipsed conformation, there is a slightly stronger repulsion between H atoms on adjacent C atoms.

► As we saw in Section 23-3, rotation does not occur around carbon-carbon double bonds at room temperature.

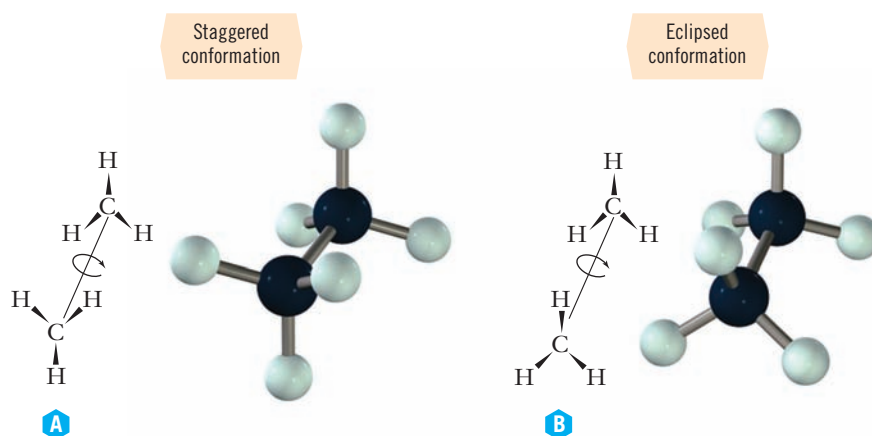
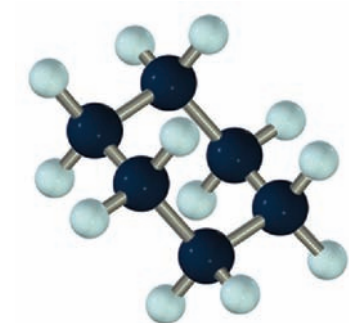
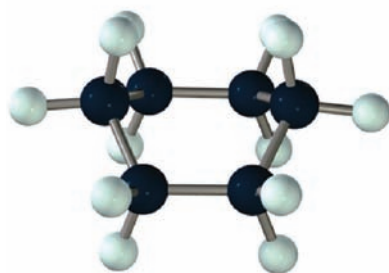


Figure 24-7 Two possible conformations of ethane. Rotation of one CH_3 group about the $C-C$ single bond, as shown by the curved arrows, converts one conformation to the other.

Unless otherwise noted, all content on this page is © Cengage Learning.



A Chair



B Boat

Figure 24-9 Two conformations of cyclohexane: (a) chair and (b) boat.



Figure 24-8 Two staggered conformations of butane, C_4H_{10} .

Consider the two conformations of butane shown in Figure 24-8. Again, staggered conformations are *slightly* more stable than eclipsed ones. Many conformations are present in a sample of butane at room temperature.

Take care to distinguish between conformational differences and isomerism. The two forms of butane shown in Figure 24-8 are *not* isomers of each other. Either form can be converted to the other by rotation about a single bond, which is a very easy process that does not involve breaking any bonds. By contrast, at least one chemical bond would have to be broken and then a new bond formed to convert one isomer to another. This is most obvious with constitutional isomerism in which a conversion would change the order of attachment of the atoms. It is also true for geometric isomers that differ in orientation about a double bond. To convert such a *cis* isomer to a *trans* isomer, it would be necessary to rotate part of the molecule about the double bond. Such a rotation would move the *p* orbitals out of the parallel alignment that is necessary to form the pi component of the double bond (see Section 8-14). This breaking of a pi bond is quite costly in terms of energy; it occurs only with the input of energy in the form of heat or light.

We saw in Section 23-1 that cyclohexane adopts a folded or “puckered” form. Cyclohexane actually exists in different stable forms, including the *chair* and *boat* forms (Figure 24-9). The chair form is the more stable of the two because, on average, the hydrogens (or other substituents) are farther from one another than in the boat form. Chair and boat cyclohexane, however, *are not* different compounds. Either form is easily converted into the other by rotation around single bonds without breaking any bonds, and the two forms cannot be separated. Thus, they are different *conformations* of cyclohexane.

Selected Reactions

Organic compounds can have quite different abilities to react, ranging from the limited reactivity of hydrocarbons and fluorocarbons to the great variety of reactions undergone by the thousands of organic molecules that contain several functional groups. Reactivity depends on structure. We can usually predict the kinds of reactions a compound can undergo by identifying the functional groups it contains.

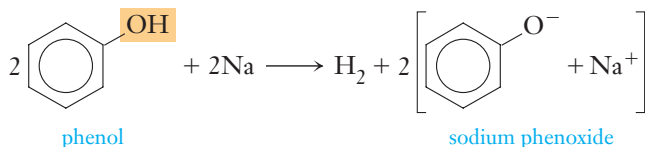
In Chapter 23, we saw three fundamental classes of organic reactions and we associated the fundamental reactions with specific functional groups. In this chapter, we will present some additional types of organic reactions.

24-4 Reactions of Brønsted–Lowry Acids and Bases

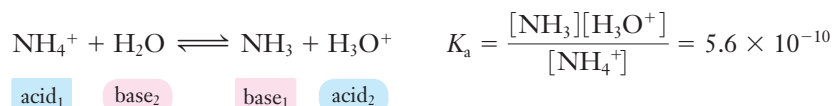
► In the Brønsted–Lowry description, an *acid* is a *proton donor* and a *base* is a *proton acceptor*. Review the terminology of conjugate acid–base pairs in Section 10-4.

Many organic compounds can act as weak Brønsted–Lowry acids or bases. Their reactions involve the transfer of H^+ ions, or *protons* (see Section 10-4). Like similar reactions of inorganic compounds, these acid–base reactions of organic acids and bases are usually fast and reversible. Consequently, we can discuss the acidic or basic properties of organic compounds in terms of equilibrium constants (see Section 18-4).

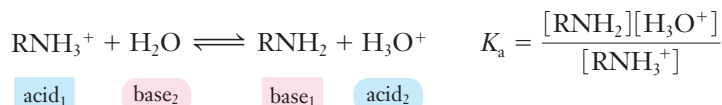
Phenols react with metallic sodium to produce *phenoxides*; the reactions are analogous to those of alcohols. Because phenols are more acidic than alcohols, their reactions are more vigorous.



We saw in Section 18-9 that salts derived from strong acids and weak bases react with water (hydrolyze) to give acidic solutions. The example given there involved the acidic character of the ammonium ion.



Similar hydrolysis reactions occur with organic ammonium salts.



We recall from Chapter 18 that the relationship $K_w = K_a K_b$ describes the acid and base strengths of any conjugate acid–base pair in aqueous solution. For instance, we can use this relationship for the $\text{CH}_3\text{NH}_3^+/\text{CH}_3\text{NH}_2$ pair. Appendix G gives K_b for methylamine, CH_3NH_2 .

$$K_{a(\text{CH}_3\text{NH}_3^+)} = \frac{K_w}{K_{b(\text{CH}_3\text{NH}_2)}} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-4}} = 2.0 \times 10^{-11}$$

In summary, we can rank the acid strengths of these classes of organic species.
carboxylic acids > phenols > substituted ammonium ions > alcohols

Our discussion has emphasized water solutions of these acids. Many organic compounds are soluble in numerous other solvents. The properties of acids and bases in other solvents depend on solvent properties such as polarity, acidity or basicity, and polarizability.

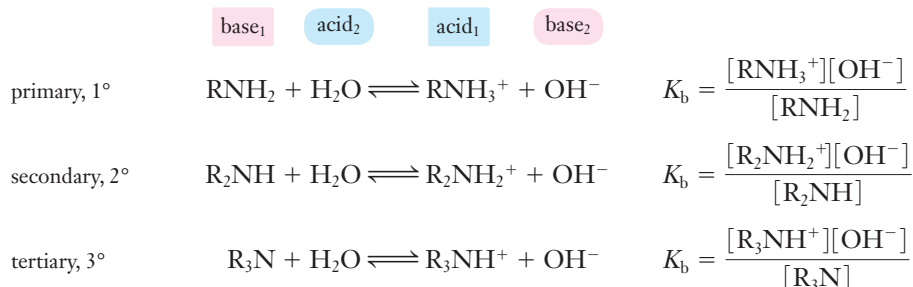
Table 24-2 Basicities of Ammonia and Some Amines In Water

Name	Formula	K_b	$\text{p}K_b$
ammonia	NH_3	1.8×10^{-5}	4.74
methylamine	CH_3NH_2	5.0×10^{-4}	3.30
dimethylamine	$(\text{CH}_3)_2\text{NH}$	7.4×10^{-4}	3.13
trimethylamine	$(\text{CH}_3)_3\text{N}$	7.4×10^{-5}	4.13
ethylamine	$\text{CH}_3\text{CH}_2\text{NH}_2$	4.7×10^{-4}	3.33
aniline	$\text{C}_6\text{H}_5\text{NH}_2$	4.2×10^{-10}	9.38
ethylenediamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	$8.5 \times 10^{-5} (K_{b1})$	4.07
pyridine	$\text{C}_5\text{H}_5\text{N}$	1.5×10^{-9}	8.82

► $\text{p}K_b = -\log K_b$
The weaker a base, the higher its $\text{p}K_b$ value.

Some Organic Bases

The most important organic bases are the amines. When dissolved in water, they are partially converted to substituted ammonium ions. This equilibrium is defined as shown in the following equations for the ionization of primary, secondary, and tertiary amines.



Most low-molecular-weight aliphatic amines are somewhat stronger bases than ammonia. Table 24-2 shows that aliphatic amines are much stronger bases than aromatic and heterocyclic amines. The basicities of amines often decrease roughly in the order tertiary > secondary > primary. Other structural factors and solvation effects, however, may outweigh this tendency, especially with tertiary amines.

Other organic bases include alkoxides, phenoxides, and carboxylates. These are the conjugate bases of weak organic acids, so their strengths decrease as the strengths of their conjugate acids increase.

We can rank the base strengths of common organic bases as

alkoxides > aliphatic amines $\approx$ phenoxides > carboxylates $\approx$ aromatic amines $\approx$ heterocyclic amines

► Primary, secondary, and tertiary amines have one, two, or three (respectively) of the H atoms of ammonia, NH_3 , replaced by organic groups (see Section 23-12).

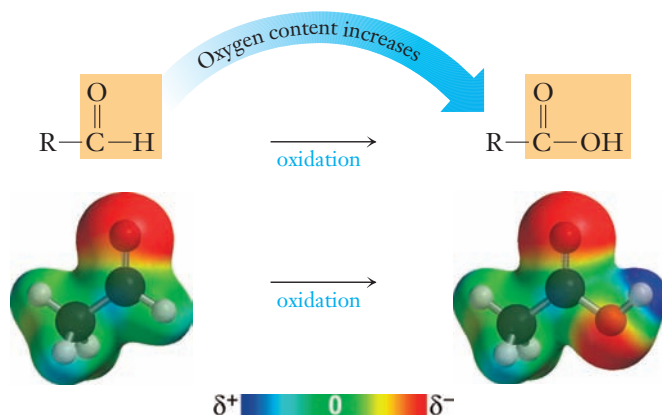


Several antibacterial mouthwashes that contain a pyridinium chloride salt.

24-5 Oxidation-Reduction Reactions

Oxidation of an organic molecule usually corresponds to *increasing* its *oxygen* content or *decreasing* its *hydrogen* content. **Reduction** of an organic molecule usually corresponds to *decreasing* its *oxygen* content or *increasing* its *hydrogen* content.

For example, the oxygen content increases when an aldehyde is converted to a carboxylic acid, so this process is an oxidation.



► We could describe the oxidation and reduction of organic compounds in terms of changes in oxidation states, just as we did for inorganic compounds in Sections 5-7 and 6-5. Formal application of oxidation state rules to organic compounds often leads to fractional oxidation states for carbon. For organic species, the descriptions in terms of increase or decrease of oxygen or hydrogen are usually easier to apply.

Converting a primary alcohol to an aldehyde and converting a secondary alcohol to a ketone are also oxidation reactions; the hydrogen content decreases.

Unless otherwise noted, all content on this page is © Cengage Learning.



CHEMISTRY IN USE

Chemical Communication

The geometries of molecules play important roles in chemical reactivity. Molecular geometry is particularly important in a group of substances known as pheromones. *Pheromones* are chemicals used for communication between members of the same species. Pheromone activity has been observed in many forms of life, from insects to humans, and pheromone research is being done at many scholarly institutions.

If you've ever observed lines of ants moving in opposite directions, you have observed the influence of pheromones on insect behavior. When an ant finds food, it immediately heads toward its nest while secreting 9-oxy-2-decenoic acid from an abdominal gland. When other ants cross this acid trail, they compulsively follow it to the food source and carry the nourishment back to their nest. Soon, many ants will be following the acid trail and reinforcing it with their own 9-oxy-2-decenoic acid secretions. Eventually, the food source becomes exhausted, trail reinforcement stops, and the acid trail evaporates. Ants are so dependent on the acid trail that if a part of it were wiped away the ants following the trail in both directions would come to a complete stop. They wouldn't know where to go.

Perhaps an even more impressive example than the total dependence on chemical communication by ants is demonstrated with the so-called "death pheromone." Immediately upon the death of an ant, fellow ants continue to groom the dead ant and treat it as if it were still living. This attention continues until the dead ant's body produces the death pheromone, 10-octadecenoic acid. On sensing this pheromone, colleagues carry the dead ant to the nearest garbage site. Interestingly, if 10-octadecenoic acid is applied to a living ant, the living ant is similarly dumped into the garbage. The discarded ant will quickly return only to be carried off again, and this process continues until the death pheromone evaporates.

Because pheromones are used by female insects to indicate their state of fertile readiness, pheromones have proven to be an effective weapon in controlling some crop-damaging insects. For example, when a specific mating pheromone is applied to crops, male cotton bollworms and female tobacco budworms compulsively mate with one another. Because of physical incompatibilities, their bodies become interlocked and both insects eventually die. Less drastic uses of pheromones to control crop damage involve baiting traps with sex pheromones to lure and trap male insects. Trapping males eventually slows reproduction, and the insect population may decrease to controllable levels. Some of these sex pheromones are so powerful that a single drop has the potential of attracting millions of males. In fact, some male insects



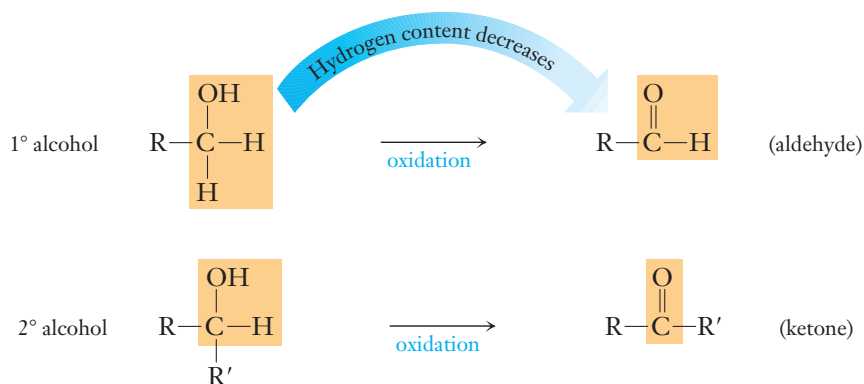
Peter Arnold/Getty Images

can detect a single molecule of female pheromone from a great distance and then successfully seek out and find the female.

Chemical communication is not confined to the insect world. Female dogs secrete the chemical *p*-hydroxybenzoate to attract males. Just like the ants and cotton bollworms, who are dependent on detecting chemicals for their actions, male dogs will attempt to mate with various objects to which *p*-hydroxybenzoate has been applied.

When we examine the molecular structures and functional groups of known pheromones, we find that they have little in common. Some pheromones contain stereoisomers, and some insects can distinguish between the stereoisomers. The structures of pheromones play vital roles in their activity. Part of the structure is an upper limit of about 20 carbon atoms. Most pheromones must diffuse through the air; those with low molecular weights are often more volatile. Scientists suspect that the physical motions of pheromone molecules, which are also a function of molecular structure, play an important role in the communication mechanism.

RONALD DELORENZO

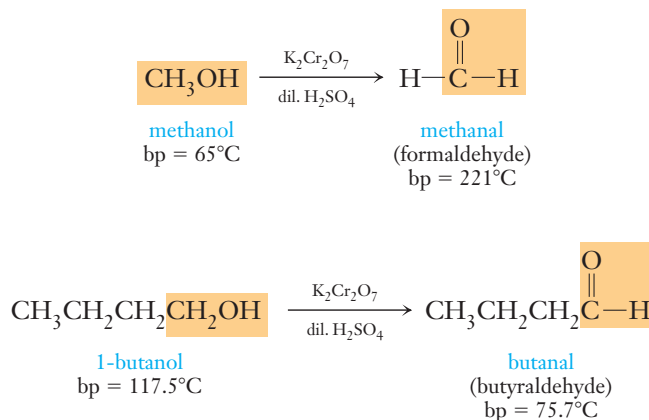


In each of these “oxidation” reactions, something else must act as the oxidizing agent (which is reduced). These oxidizing agents are often inorganic species such as dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$. The reverse of each of the preceding reactions is a reduction of the organic molecule. In this reverse reaction, the reducing agent (the substance that is oxidized) is often an inorganic compound.

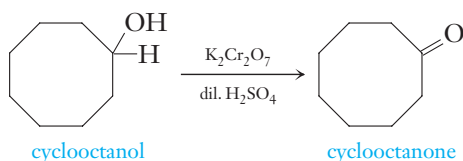
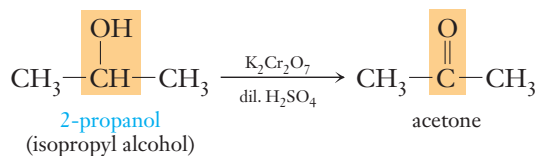
Let us look at a few other important types of organic oxidations and reductions.

Oxidation of Alcohol

Aldehydes can be prepared by the oxidation of *primary* alcohols. The reaction mixture is heated to a temperature slightly above the boiling point of the aldehyde so that the aldehyde distills out as soon as it is formed. Potassium dichromate in the presence of dilute sulfuric acid is the common oxidizing agent.



Ketones can be prepared by the oxidation of *secondary* alcohols. Ketones are not as susceptible to oxidation as are aldehydes.



► The notation R' emphasizes that the two R groups may be the same ($\text{R} = \text{R}'$, e.g., in the formation of

acetone, $\text{CH}_3-\overset{\text{O}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$) or different ($\text{R} \neq \text{R}'$, e.g., in the formation of methyl ethyl ketone, $\text{CH}_3-\overset{\text{O}}{\underset{\text{CH}_2\text{CH}_3}{\text{C}}}-\text{H}$).

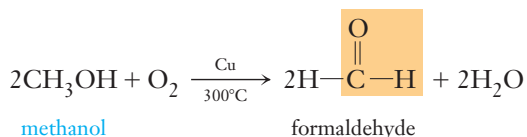
► Aldehydes are easily oxidized to carboxylic acids. They must therefore be removed from the reaction mixture as soon as they are formed. Aldehydes have lower boiling points than the alcohols from which they are formed, so the removal of aldehydes can be accomplished if conditions such as temperature and pressure are carefully controlled.

► Ketones are not as easily oxidized as aldehydes, because oxidation of a ketone requires the breaking of a carbon-carbon bond. Thus, it is not as important that they be quickly removed from the reaction mixture.

► These reactions can also be described as a type of *elimination* reaction (see Section 23-18). Two hydrogen atoms are eliminated to form a $\text{C}=\text{O}$ double bond.

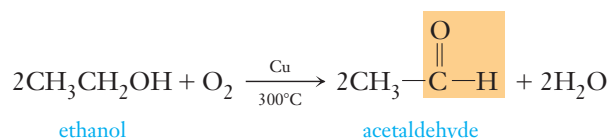
Unless otherwise noted, all content on this page is © Cengage Learning.

Aldehydes and ketones can be prepared by a catalytic process that involves passing alcohol vapors and air over a copper gauze or powder catalyst at approximately 300°C. Here the oxidizing agent is O₂.



Formaldehyde is quite soluble in water; the gaseous compound can be dissolved in water to give a 40% solution.

Acetaldehyde can be prepared by the similar oxidation of ethanol.

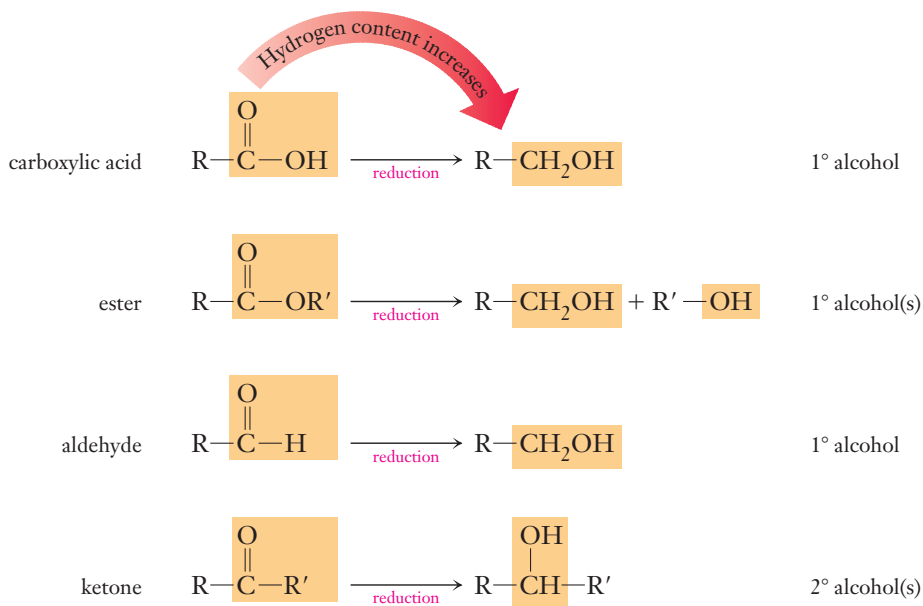


Oxidation of tertiary alcohols is difficult because the breaking of a carbon–carbon bond is required. Such oxidations are of little use in synthesis.

Reduction of Carbonyl Compounds

Reduction of a variety of compounds that contain the carbonyl group provides synthetic methods to produce primary and secondary alcohols. Lithium aluminum hydride, LiAlH₄, is capable of reducing the carboxyl group of carboxylic acids and esters and the carbonyl group of aldehydes and ketones to produce various alcohols. Sodium borohydride, NaBH₄, is a less reactive reducing agent that can be used to reduce aldehydes and ketones (carbonyl groups), but not acids and esters (carboxyl groups).

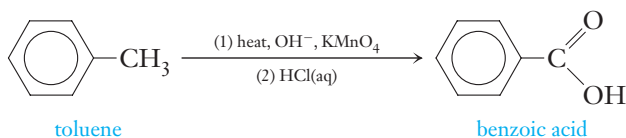
► Organic reactions are sometimes written in extremely abbreviated form. This is often the case when a variety of common oxidizing or reducing agents will accomplish the desired conversion.



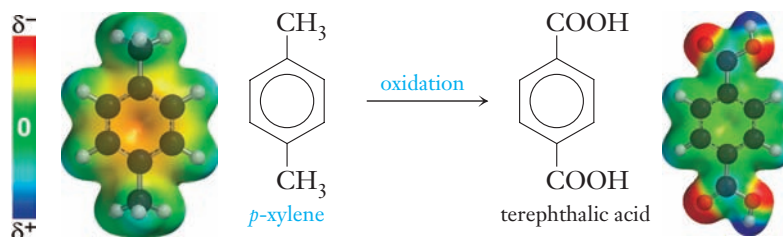
Oxidation of Alkylbenzenes

Unsubstituted aromatic hydrocarbons (see Sections 23-5 and 23-6) are quite resistant to oxidation by chemical oxidizing agents. The reactions of strong oxidizing agents with alkylbenzenes illustrate the stability of the benzene ring system. Heating toluene with a ba-

sic solution of KMnO_4 results in a nearly 100% yield of benzoic acid. The ring itself remains intact; only the nonaromatic portion of the molecule is oxidized.



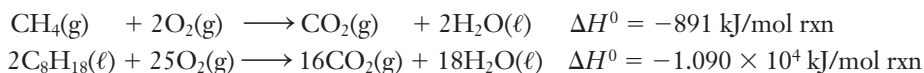
Two such alkyl groups on an aromatic ring are oxidized to give a diprotic acid, as the following example illustrates.



Terephthalic acid is used to make polyesters, an important class of polymers (see Section 23-19).

Combustion of Organic Compounds

The most extreme oxidation reactions of organic compounds occur when they burn in O_2 . Such *combustion reactions* (see Section 5-9) are highly exothermic. When complete combustion takes place in excess O_2 , the products are CO_2 and H_2O . Examples of alkane combustions are



► Recall that ΔH^0 is negative for an exothermic process.

The **heat of combustion** is the amount of energy *liberated* per mole of substance burned. Heats of combustion are assigned positive values *by convention* (Table 24-3) and are therefore equal in magnitude, but opposite in sign, to ΔH^0 values for combustion reactions. The combustion of hydrocarbons produces large volumes of CO_2 and H_2O gas in addition to large amounts of heat. The rapid formation and expansion of these gases at high temperature and pressure drive the pistons or turbine blades in internal combustion engines.

In the absence of sufficient oxygen, partial combustion of hydrocarbons occurs. The products may be carbon monoxide (a very poisonous gas) or carbon (which deposits on spark plugs, in the cylinder head, and on the pistons of automobile engines). Modern automobile

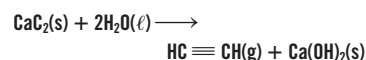
Table 24-3 Heats of Combustion of Some Alkanes

Hydrocarbon		Heat of Combustion	
		kJ/mol	J/g
methane	CH_4	891	55.7
propane	C_3H_8	2220	50.5
pentane	C_5H_{12}	3507	48.7
octane	C_8H_{18}	5450	47.8
decane	$\text{C}_{10}\text{H}_{22}$	6737	47.4
ethanol*	$\text{C}_2\text{H}_5\text{OH}$	1372	29.8

*Not an alkane, but often added to automobile fuels; included here for comparison.



Acetylene is produced by the slow addition of water to calcium carbide.



The light of one kind of headlamp used by miners and cave explorers is given off by the combustion of acetylene.

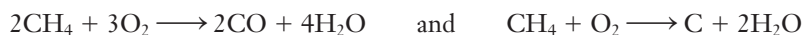
Unless otherwise noted, all content on this page is © Cengage Learning.



Charles Steele

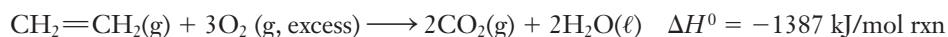
Hexane, C_6H_{14} , an alkane, burns cleanly in air to give CO_2 and H_2O (top). 1-Hexene, C_6H_{12} , an alkene, burns with a flame that contains soot (middle). Burning *o*-xylene, an aromatic hydrocarbon, produces large amounts of soot (bottom).

engines use sensors and microcomputer chips to control the air supply and to optimize the fuel/ O_2 ratio. The reactions of methane with insufficient oxygen are



All hydrocarbons undergo similar reactions.

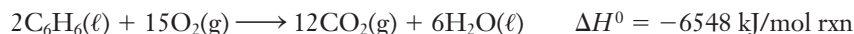
The alkenes, like the alkanes, burn in *excess* oxygen to produce carbon dioxide and water in exothermic reactions.



When an alkene (or any other unsaturated organic compound) is burned in air, a yellow, luminous flame is observed, and considerable soot (unburned carbon) is formed. This reaction provides a qualitative test for unsaturation. Saturated hydrocarbons burn in air without forming significant amounts of soot.

Acetylene lamps are charged with calcium carbide. Very slow addition of water produces acetylene, which is burned as it is produced. Acetylene is also used in the oxyacetylene torch for welding and cutting metals. When acetylene is burned with oxygen, the flame reaches temperatures of about 3000°C .

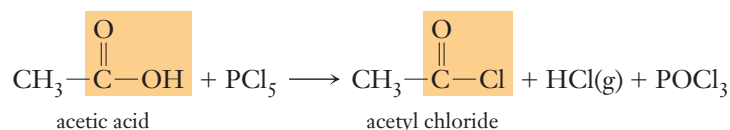
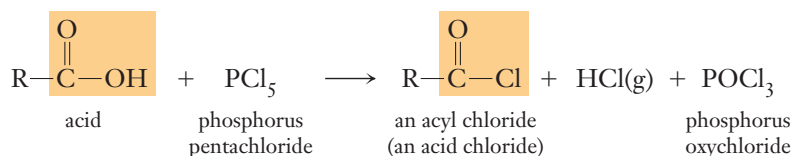
Like other hydrocarbons, the *complete combustion* of aromatic hydrocarbons, such as benzene, releases large amounts of energy.



Because they are so unsaturated, aromatic hydrocarbons burn *in air* with a yellow, sooty flame.

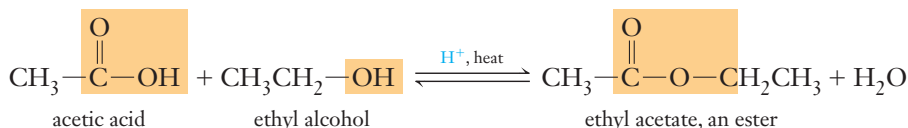
24-6 Formation of Carboxylic Acid Derivatives

The carboxylic acid derivatives introduced in Section 23-14 can be formed by *substitution* of another group in place of the $-OH$ in the carboxyl group. The acyl halides (acid halides) are usually prepared by treating acids with PCl_3 , PCl_5 , or $SOCl_2$ (thionyl chloride). In general terms, the reaction of acids with PCl_5 may be represented as

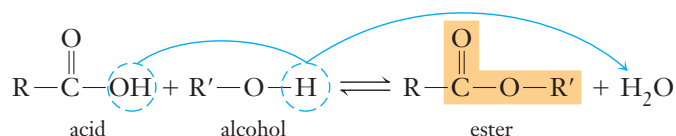


The acyl halides are much more reactive than their parent acids. Consequently, they are often used in reactions to introduce an acyl group into another molecule.

When an organic acid is heated with an alcohol, an equilibrium is established with the resulting *ester* and water. The reaction is catalyzed by traces of strong inorganic acids, such as a few drops of concentrated H_2SO_4 .



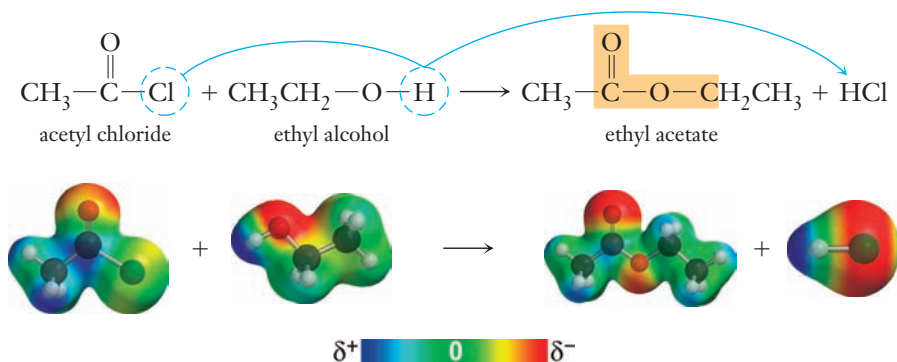
In general terms, the reaction of an organic acid and an alcohol may be represented as



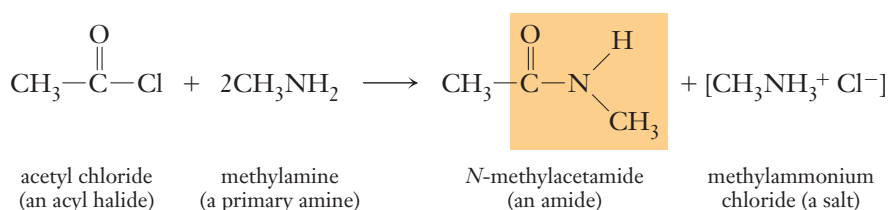
► Many experiments have shown conclusively that the OH group from the acid and the H from the alcohol are the atoms that form water molecules.

(R and R' may be the same or different groups.)

Reactions between acids and alcohols are usually quite slow and require prolonged boiling (refluxing). The reactions between most acyl halides and most alcohols, however, occur very rapidly without requiring the presence of an acid catalyst.



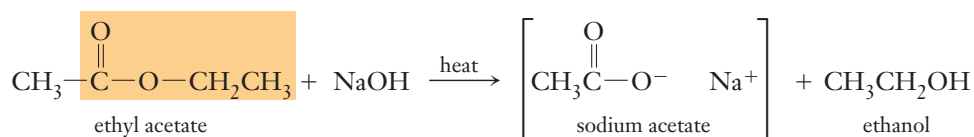
Amides are usually *not* prepared by the reaction of an amine with an organic acid. Acyl halides react readily with primary and secondary amines to produce amides. The reaction of an acyl halide with a primary or secondary amine produces an amide and a salt of the amine.



► In this preparation, half of the amine is converted to an amide and the other half to a salt.

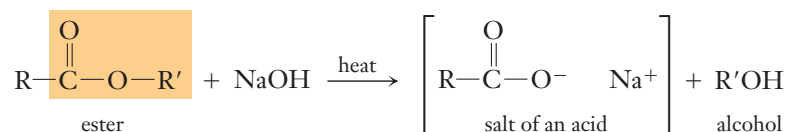
24-7 Hydrolysis of Esters

Because most esters are not very reactive, strong reagents are required for their reactions. Esters can be hydrolyzed by refluxing them with solutions of strong bases.



The hydrolysis of esters in the presence of strong bases is called **saponification** (soap-making).

In general terms, the hydrolysis of esters may be represented as

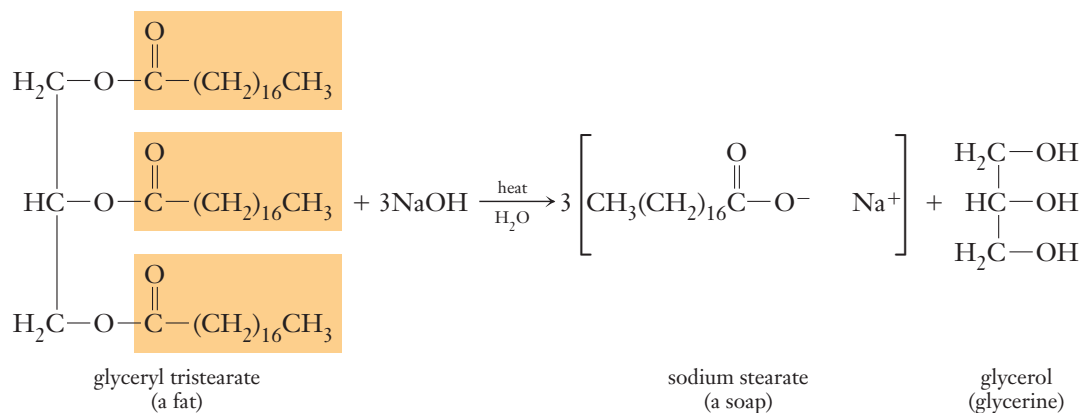


Unless otherwise noted, all content on this page is © Cengage Learning.



Soap can be made by boiling animal fat (glyceryl tristearate) with an alkaline solution obtained from the ashes of hardwood. The resulting soap can be “salted out” by adding sodium chloride, making use of the fact that soap (containing sodium stearate) is less soluble in a salt solution than in water.

Like other esters, fats and oils (see Section 23-14) can be hydrolyzed in strongly basic solution to produce salts of the acids and the trihydric alcohol glycerol. The resulting alkali metal salts (commonly sodium or potassium) of long-chain fatty acids are **soaps**. In Section 14-18, we described the cleansing action of soaps and detergents.



Biopolymers

As we study the molecules and ions in living organisms such as humans, we learn that substances with a huge range of sizes and complexities are involved. These include small molecules and ions such as sodium ions, trace metals, ketones, alcohols, and carboxylic acids. Steroids, hormones, vitamins, fats, and oils are somewhat larger. As we continue up the scale of sizes of substances present in living systems, we encounter the mammoth polymers

(biopolymers, or polymers found in biological systems). Concepts discussed in the first 23 chapters and the first half of this chapter can be applied to large molecules and ions as well as small ones. In the following sections, we will look briefly at three classes of biopolymers (carbohydrates, proteins, and nucleic acids), keeping in mind that almost all of the chemical concepts used in these discussions were introduced earlier in this text.

24-8 Carbohydrates

Carbohydrates have the general formula $C_n(H_2O)_m$, thus the name hydrated carbons or, more commonly, carbohydrates. **Monosaccharides**, or simple sugars, are the monomers from which more complex carbohydrates are constructed. The most important simple sugars contain either five or six carbon atoms. Monosaccharides that contain an aldehyde group are called **aldoses**, and those that contain a ketone group are called **ketoses**. The most commonly encountered natural monosaccharide is D-glucose, $C_6H_{12}O_6$, also known as dextrose or blood sugar. Figure 24-10a shows glucose as it is often written to emphasize its aldehyde functional group. We can see from this formula that carbons 2, 3, 4, and 5 in glucose each are bonded to four *different* groups and are, therefore, chiral. Each different monosaccharide has a unique arrangement of atoms about its chiral atoms. Some important monosaccharides are shown in Table 24-4.

In addition to their aldehyde or ketone form, saccharides can also exist in a cyclic form. Figure 24-10 shows the interconversion of glucose between its linear form and its cyclic form. Figure 24-10b shows the molecule rotated into a conformation that brings the hydroxyl group of carbon 5 near the aldehyde carbon. In this conformation, a reversible reaction occurs in which a hydrogen is moved from the hydroxyl group to the carbonyl

► The word *saccharide* comes from the Latin *saccharum*, for “sugar” or “sweet.”

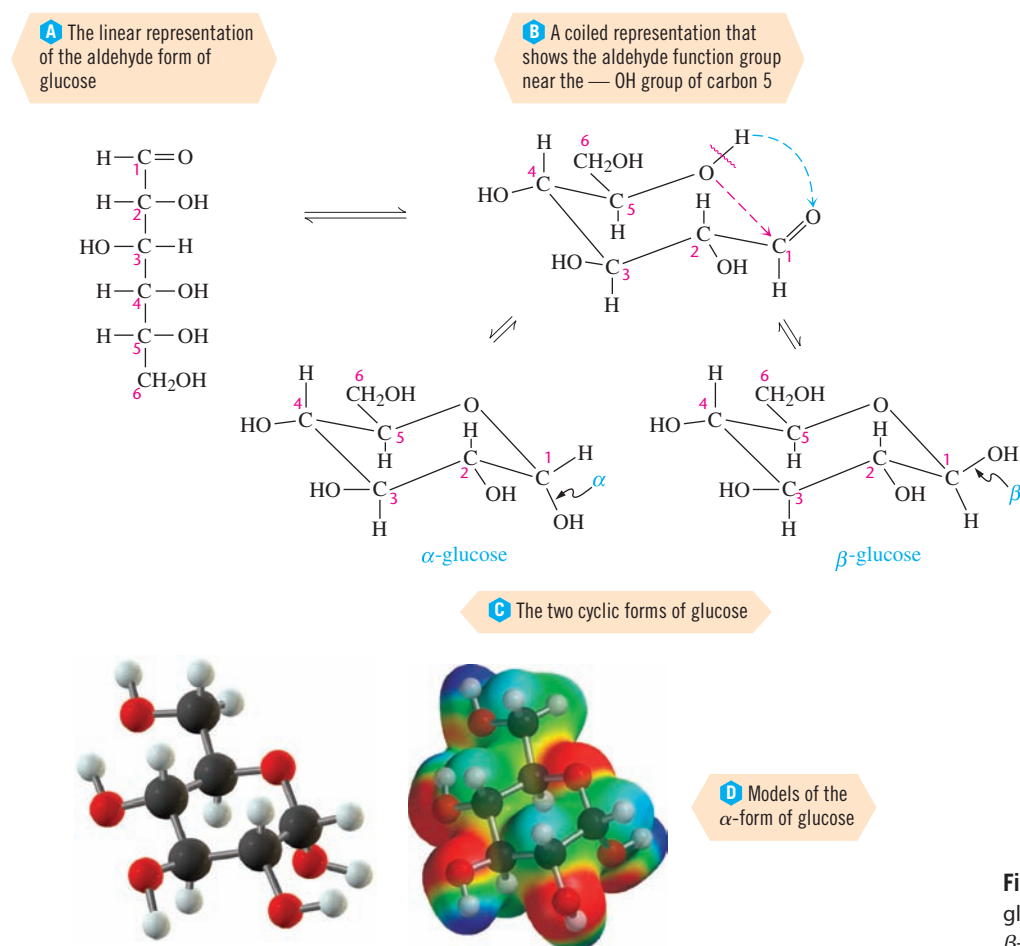


Figure 24-10 The cyclization of glucose to form either the α - or the β -cyclic form.

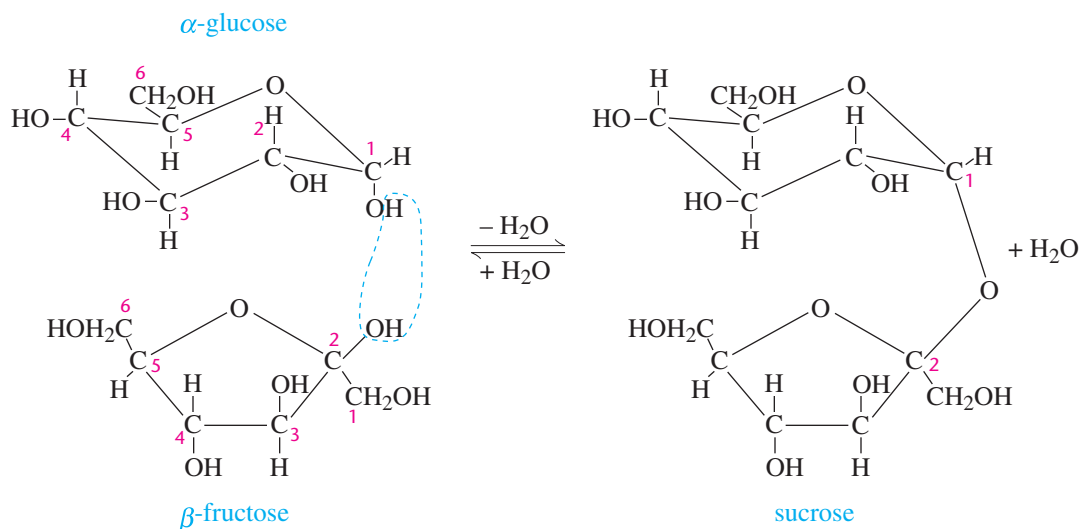
Unless otherwise noted, all content on this page is © Cengage Learning.

Table 24-4 Some Important Monosaccharides

Monosaccharides with Five Carbon Atoms			
$ \begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $ ribose	$ \begin{array}{c} \text{CHO} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $ arabinose	$ \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C}=\text{O} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $ ribulose	
Monosaccharides with Six Carbon Atoms			
$ \begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $ glucose	$ \begin{array}{c} \text{CHO} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $ mannose	$ \begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $ galactose	$ \begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C}=\text{O} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array} $ fructose

oxygen and an ether bond is formed between the two carbons (see Figure 24-10c). During the formation of the ether bond, a ring is also formed and carbon atom 1 becomes chiral. This new chiral center can exist as either of two optical isomers; the resulting stereoisomers are referred to as α - or β -forms.

Most naturally occurring carbohydrates contain more than one monosaccharide unit. Complex carbohydrates are formed when two or more monosaccharides are linked. This linkage between two monosaccharides occurs by elimination of a molecule of water and the formation of an ether bond between two of the cyclic structures, as shown in Figure 24-11. The newly formed C—O bond linking the rings is called the **glycosidic bond**. Figure 24-11 illustrates the linkage of α -glucose and β -fructose to form sucrose. Fructose is a ketone-containing carbohydrate that exists in the cyclic form shown. A **disaccharide** is a molecule consisting of two monosaccharides joined together by a glycosidic bond. Sucrose is a disaccha-

**Figure 24-11** Formation of sucrose by the condensation of an α -glucose molecule with a β -fructose molecule.

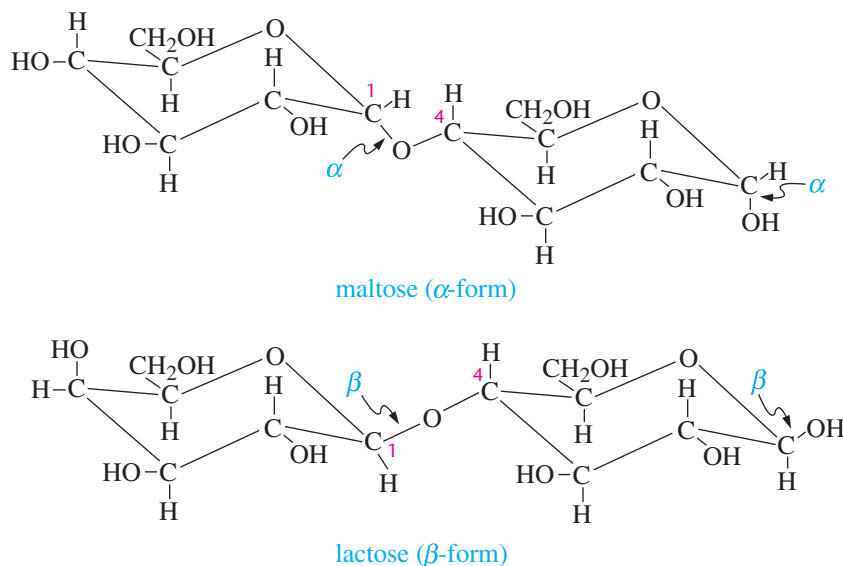


Figure 24-12 Two disaccharides: maltose and lactose. Each involves two monosaccharide units. Maltose has an α -1,4-linkage and lactose has a β -1,4-linkage.

ride; two other disaccharides, each involving only glucose units, are shown in Figure 24-12. In such a molecule, the C—O—C linkage between the monosaccharide units involves carbon number 1 or 2 of one monosaccharide and carbon number 1, 4, or 6 of the other monosaccharide. The arrangement about the carbon number 1 or 2 is what is described as the α - or β -linkage. Using these notations, we describe maltose as consisting of two glucose units joined by an α -1,4-linkage. Lactose has a β -1,4-linkage. Table 24-5 lists some of the common sugars.

A carbohydrate that contains three monosaccharides is called a **trisaccharide**, and so on. Carbohydrates that contain from four to ten monosaccharides are usually called by the general term **oligosaccharides**. Carbohydrates that contain still larger numbers of monosaccharide units are called **polysaccharides**.

Amylose, a type of starch found in plants, is a polysaccharide. It consists of a linear combination of several thousand glucose units joined by α -1,4-linkages. In our bodies, we store glucose in a form known as amylopectin, or glycogen. Glycogen is similar to amylose; it can contain up to 100,000 glucose monomers with the majority linked via an α -1,4-linkage. Unlike amylose, it contains occasional branches via α -1,6-linkages. In Figure 24-13, each sphere represents a glucose unit. All links are α -1,4 except where branching takes place; branching utilizes an α -1,6-linkage. Our digestive systems contain enzymes (see Sections 16-9 and 24-9) that can break this biopolymer, glycogen, into its monomeric glucose units as we need energy to drive other biological processes.

Cellulose, the structural biopolymer found in plants, contains the β -1,4-linkage of glucose units. Our digestive systems are incapable of breaking the β -1,4-linkage, so we cannot utilize cellulose as a source of stored glucose. Some animals such as termites and cattle are able to digest cellulose.

► Glycogen provides the main short-term energy storage in many animal cells.

Table 24-5 Sweetness of Common Sugars Relative to Sucrose

Substance	Sweetness Relative to Sucrose at 1.00
lactose (milk sugar, a disaccharide)	0.16
galactose (a monosaccharide in milk sugar)	0.32
maltose (a disaccharide used in beer making)	0.33
glucose (dextrose, a common monosaccharide)	0.74
sucrose (table sugar, a disaccharide)	1.00
fructose (fruit sugar, a monosaccharide)	1.74

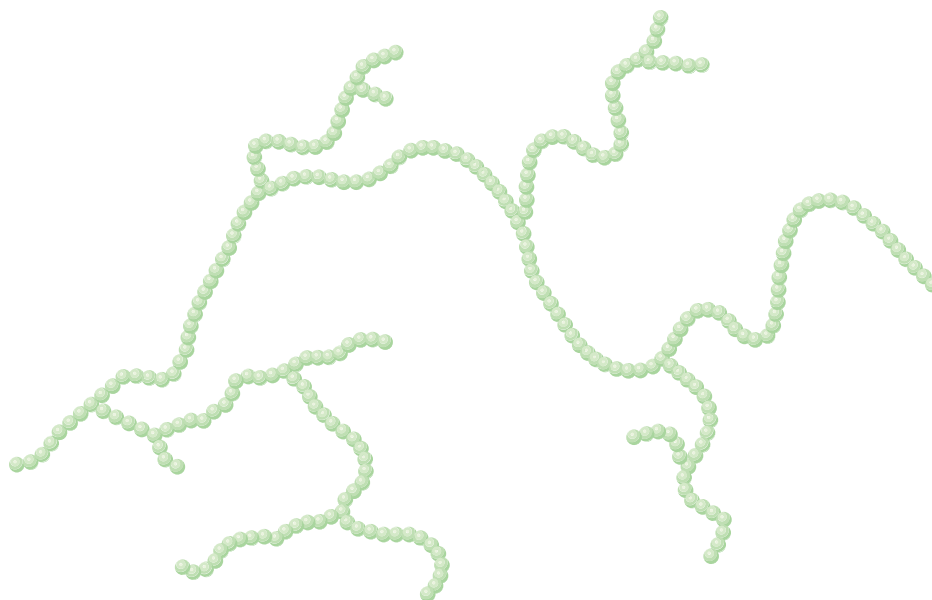


Figure 24-13 A small portion of amylopectin, or glycogen (a biopolymer).

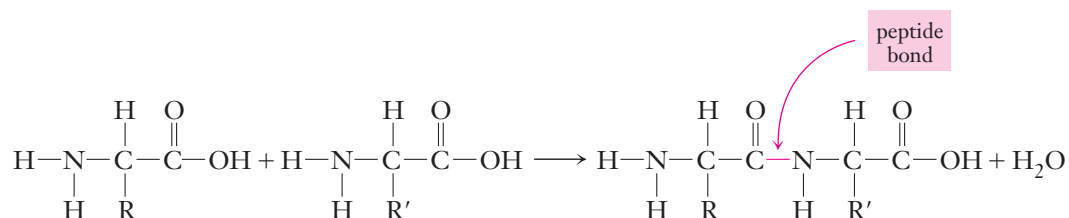


Bacteria in the digestive tracts of termites and cattle produce an enzyme that allows them to digest the cellulose in wood and grass.



24-9 Polypeptides and Proteins

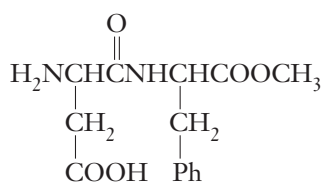
Two amino acids can react to form an amide bond (see Section 23-19). Compounds formed by the linking of small numbers of amino acids are called **peptides**, and the amide bond linking the amino acid monomers is called the **peptide bond**.



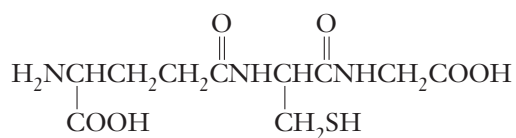
The prefixes di-, tri-, and so on are used to indicate the number of amino acid monomers that are joined to form the peptide. The peptide indicated in the preceding equation is a **dipeptide**.

Twenty different α -amino acids (see Section 23-13) are found widely in nature. Each amino acid is commonly given a three-letter abbreviation. These acids differ in the R groups attached to the α -carbon (the carbon adjacent to the —COOH group). Differences in R groups lead to differences in the properties of the α -amino acids. The amino acids are usually classified by their R groups, or side chains, according to two criteria. The first classification depends on whether the R groups are polar or nonpolar; the second describes whether the R group contains an acidic or basic group. The 20 common amino acids are shown, according to these classifications, in Table 24-6.

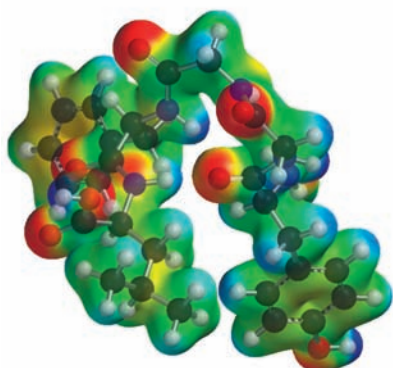
Many small peptides are known to have physiological significance. Aspartame, a common artificial sweetener, is a dipeptide. Glutathione, a tripeptide, acts as a scavenging agent for harmful oxidizing agents believed to cause cancer. Enkephalins, which are naturally occurring analgesics (pain relievers) that occur in the brain, are pentapeptides. The antibiotics gramicidin-S and tyrocidine-A are cyclic decapeptides (i.e., they contain ten amino acids linked into a ring by peptide bonds) produced by a bacterium.



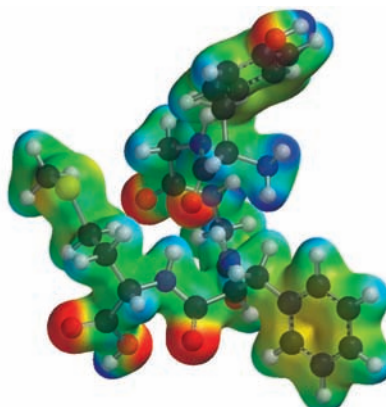
aspartame
(Asp-Phe-OCH₃)



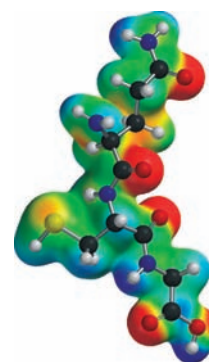
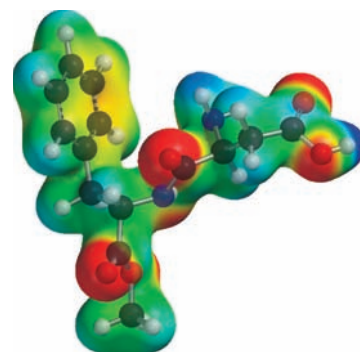
glutathione
(Gln-Cys-Gly)



Tyr-Gly-Gly-Phe-Leu
leucine enkephalin



Tyr-Gly-Gly-Phe-Met
methionine enkephalin



δ^+  δ^-
Models of aspartame (top) and glutathione (bottom).

A **protein** is a biopolymer, of molecular weight typically 5000 g/mol or greater, consisting of one or more polypeptide chains. The α -amino acids that occur in nearly all proteins are the L-optical isomer.

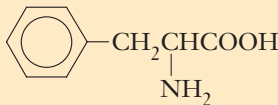
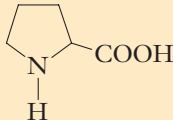
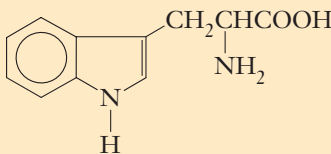
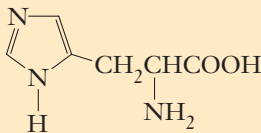
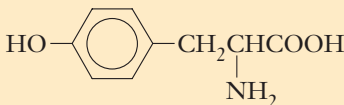
► Some organisms such as bacteria also produce D-amino acids.

An **enzyme** is a protein that catalyzes a biological reaction.

Each protein consists of one or more polypeptide chains with a unique sequence of amino acids. The order of these monomers is termed the **primary structure** of the protein. The many possible interactions between different amino acids in the polypeptide chain cause each protein molecule to adopt a characteristic shape, usually depending on its environment. The *secondary structure* of a protein is the arrangement in space of the polypeptide backbone, without reference to the conformations of the side chains (R groups). Myoglobin is the

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 24-6 The 20 Common Amino Acids Found in Proteins

Nonpolar R Groups			
alanine (Ala)	CH_3CHCOOH NH_2	phenylalanine (Phe)	
glycine (Gly)	HCHCOOH NH_2	proline (Pro)	
isoleucine (Ile)	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHCOOH}$ NH_2	tryptophan (Trp)	
leucine (Leu)	$(\text{CH}_3)_2\text{CHCH}_2\text{CHCOOH}$ NH_2		
methionine (Met)	$\text{CH}_3\text{SCH}_2\text{CH}_2\text{CHCOOH}$ NH_2	valine (Val)	$(\text{CH}_3)_2\text{CHCHCOOH}$ NH_2
Polar, Neutral R Groups			
asparagine (Asn)	$\text{H}_2\text{N}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2\text{CHCOOH}$ NH_2	serine (Ser)	$\text{HOCH}_2\text{CHCOOH}$ NH_2
glutamine (Gln)	$\text{H}_2\text{N}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2\text{CH}_2\text{CHCOOH}$ NH_2	threonine (Thr)	$\text{CH}_3\text{CH}(\text{OH})\text{CHCOOH}$ NH_2
Polar, Acidic R Groups		Polar, Basic R Groups	
aspartic acid (Asp)	$\text{HOOCCH}_2\text{CHCOOH}$ NH_2	arginine (Arg)	$\text{H}_2\text{N}-\overset{\text{NH}}{\parallel}\text{C}-\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CHCOOH}$ NH_2
glutamic acid (Glu)	$\text{HOOCCH}_2\text{CH}_2\text{CHCOOH}$ NH_2	histidine (His)	
cysteine (Cys)	$\text{HSCH}_2\text{CHCOOH}$ NH_2	lysine (Lys)	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCOOH}$ NH_2
tyrosine (Tyr)			

oxygen-storing protein in muscles. Its amino acid sequence (primary structure) and a three-dimensional representation of its secondary structure are shown in Figure 24-14. The *tertiary structure* of a protein describes the overall shape of the protein, including the side chains and any other nonpeptide components of the protein. Myoglobin is referred to as a globular protein. Some proteins consist of multiple polypeptide units called *subunits*. These subunits are held to one another by noncovalent interactions such as hydrogen bonding, dipole–dipole interactions, or ionic attractions to form the *quaternary structure* of the protein.

Val-Leu-Ser-Glu-Gly-Glu-Trp-Gln-Leu-Val-Leu-His-Val-Trp-Ala-Lys-Val-
 Glu-Ala-Asp-Val-Ala-Gly-His-Gly-Gln-Asp-Ile-Leu-Ile-Arg-Leu-Phe-Lys-
 Ser-His-Pro-Glu-Thr-Leu-Glu-Lys-Phe-Asp-Arg-Phe-Lys-His-Leu-Lys-
 Thr-Glu-Ala-Glu-Met-Lys-Ala-Ser-Glu-Asp-Leu-Lys-Lys-His-Gly-Val-Thr-
 Val-Leu-Thr-Ala-Leu-Gly-Ala-Ile-Leu-Lys-Lys-Lys-Gly-His-His-Glu-Ala-
 Glu-Leu-Lys-Pro-Leu-Ala-Gln-Ser-His-Ala-Thr-Lys-His-Lys-Ile-Pro-Ile-Lys-
 Tyr-Leu-Glu-Phe-Ile-Ser-Glu-Ala-Ile-Ile-His-Val-Leu-His-Ser-Arg-His-
 Pro-Gly-Asn-Phe-Gly-Ala-Asp-Ala-Gln-Gly-Ala-Met-Asn-Lys-Ala-Leu-
 Glu-Leu-Phe-Arg-Lys-Asp-Ile-Ala-Ala-Lys-Tyr-Lys-Glu-Leu-Gly-Tyr-Gln-Gly

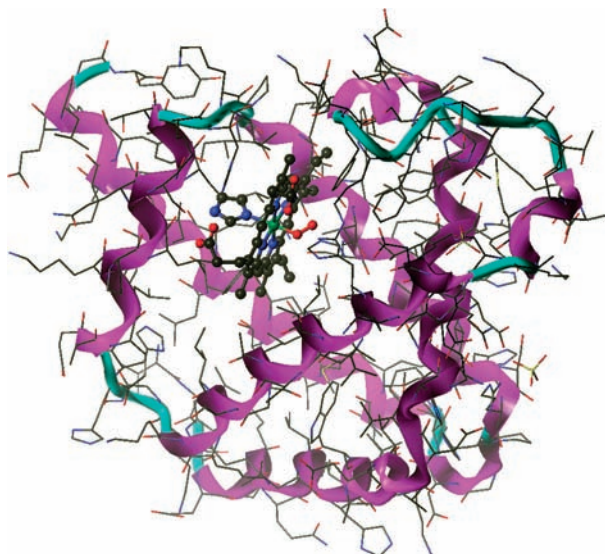
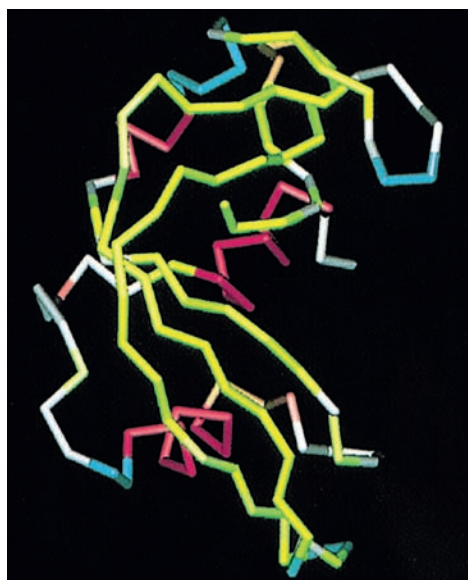


Figure 24-14 The amino acid sequence and the three-dimensional representation of myoglobin, the oxygen-storing protein in muscles.

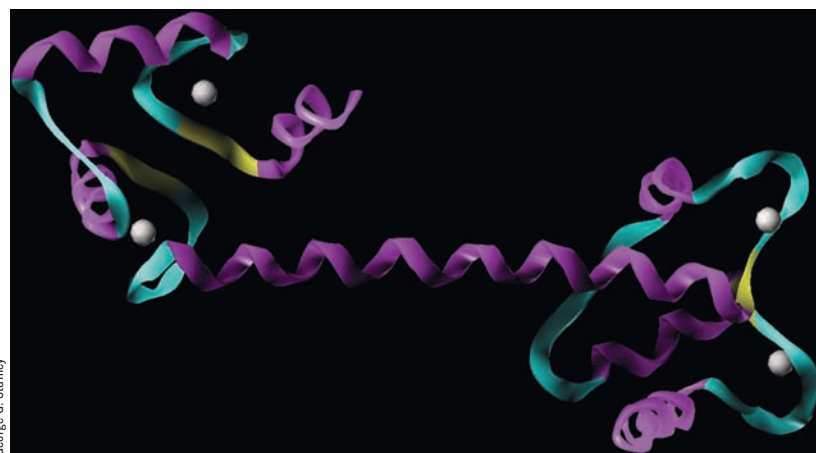
The folding and coiling patterns of a protein often affect its biological activity, for instance, its effectiveness as an enzyme. Heat and the ionic environment can alter the pattern of folding and coiling, causing the enzyme or protein to become inactive, or *denatured*.

Proteins make up more than 50% of the dry weight of animals and bacteria. They perform many important functions in living organisms, a few of which are indicated in Table 24-7. Each protein carries out a specific biochemical function. Each is a polypeptide with its own unique *sequence* of amino acids. The amino acid sequence of a protein determines exactly how it folds up in a three-dimensional conformation and how it performs its precise biochemical task.



Brent Iverson

A model of the peptide chain of the protein ribonuclease A. In this representation, the amino acids that form the backbone are shown as sticks. The different colors represent regions within the folding and coiling patterns.



George G. Stanley

A “ribbon” model of the protein calmodulin. In this type of model, the ribbon represents the polypeptide chain. This protein coordinates with Ca^{2+} ions (white spheres) and aids in transporting them in living systems.

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 24-7 Some Functions of Proteins

Example	Function
Enzymes	
amylase	converts starch to glucose
DNA polymerase I	repairs DNA molecule
transaminase	transfers amino group from one amino acid to another
Structural Proteins	
viral coat proteins	outer covering of virus
keratin	hair, nails, horns, hoofs
collagen	tendons, cartilage
Hormones	
insulin, glucagon	regulate glucose metabolism
oxytocin	regulates milk production in female mammals
vasopressin	increases retention of water by kidney
Contractile Proteins	
actin	thin contractile filaments in muscle
myosin	thick filaments in muscle
Storage Proteins	
casein	a nutrient protein in milk
ferritin	stores iron in spleen and egg yolk
Transport Proteins	
hemoglobin	carries O ₂ in blood
myoglobin	carries O ₂ in muscle
serum albumin	carries fatty acids in blood
cytochrome <i>c</i>	transfers electrons
Immunological Proteins	
γ -globulins	form complexes with foreign proteins
Toxins	
neurotoxin	blocker of nerve function in cobra venom
ricin	nerve toxin from castor beans (most toxic substance known—0.000005 g is fatal to humans)

24-10 Nucleic Acids

We have seen that polysaccharides are polymers composed of a single type of monomer (carbohydrates), as are proteins (amino acids). The third type of biopolymer is more complex. Nucleic acids use three very different types of monomers: the phosphate group, one of two simple carbohydrate units (*ribose* or *deoxyribose*), and selected organic bases (Figure 24-15). A typical segment of the resulting polymer is shown in Figure 24-16.

There are two types of nucleic acids: **ribonucleic acid (RNA)** and **deoxyribonucleic acid (DNA)**. One of the ways in which they differ is in the carbohydrate that they contain. The two carbohydrates in nucleic acids are **ribose** (contained in RNA) and **2-deoxyribose** (contained in DNA); these carbohydrates differ in the presence or absence of an oxygen atom on carbon 2.

The Cells' Drinking Straws

Proteins, enzymes, and other biological structures are small enough to be considered large molecules. Yet, they are responsible for performing physical bodily tasks such as transporting nutrients and wastes and serving as barriers in organ walls. How are important chemicals such as water and metal ions actually moved from place to place inside the body? The 2003 Nobel Prize in Chemistry was awarded to two scientists who are helping us to understand how these materials pass in and out of cells.

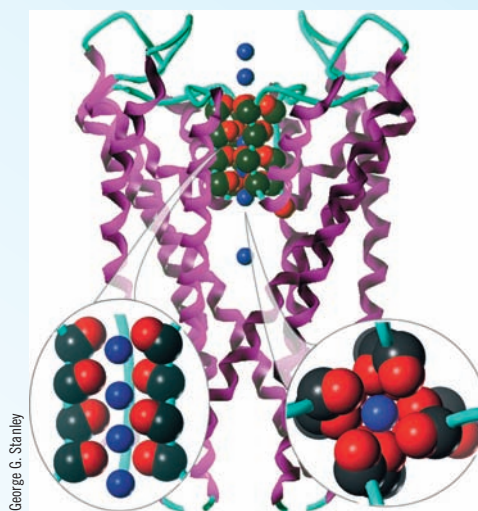
Cell membranes are composed of proteins—large, chainlike molecules constructed of repeating amino acid units. These proteins are predominantly lipophilic (repellent to polar species), which prevents the cell's contents from leaking through the membrane and mixing with the surrounding environment. The complex structures of protein molecules allow them to self-organize into three-dimensional structures. Within these structures, areas of relatively high polarity (such as clumps of carbon–oxygen bonds or charged R groups) can function as “channels” for the passage of small polar molecules and ions.

Dr. Peter Agre studied membrane channels that allow water to enter and exit cells without admitting H_3O^+ ions. Cells require water to regulate their volume and osmotic pressure. However, because the cells store energy by maintaining a charge differential from their surroundings, proton loss through the channel as H_3O^+ must be prevented.

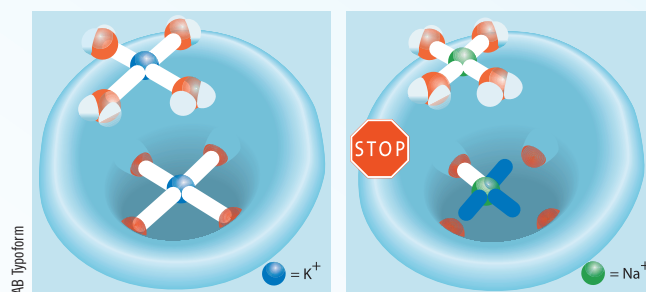
Agre isolated a suspected water-channel protein and demonstrated its function with a simple experiment: introducing it into test cells that were then submerged in aqueous solutions, forcing them to absorb water and rupture. X-ray crystallographic analysis of this protein revealed the atomic logic behind the water channel's selectivity. As H_2O molecules and H_3O^+ ions travel down the channel, they encounter a narrow area where the protein's amino acid units are in particularly close proximity. This 2.8-Å-wide “doorway” is small enough so that only water molecules can fit through it. Two of the amino acid units located nearby have R groups bearing positive charges, so electrostatic repulsion also helps to block H_3O^+ passage. Proteins that contain water channels are called *aquaporins*; their malfunction has been linked to fluid retention, dehydration, diabetes, and kidney disease.

Cellular metal ion transport is biologically important because our muscular and nervous systems are regulated by charged species. Cells use membrane channels to extract potassium ions selectively from environments containing both K^+ and Na^+ . Because the K^+ ion is *larger* than the Na^+ ion, this process cannot be accomplished by simply restricting the channel diameter. Dr. Roderick MacKinnon showed that potassium selectivity arises from a preferential interaction between the potassium cation and the atoms of the protein amino acids composing the channel walls.

K^+ and Na^+ ions initially enter the ion channel as solvated species, encased in shells of H_2O molecules. However, they must eventually shed their water to pass through narrow rings of



Tube-and-ribbon representation of the X-ray structure of a potassium ion channel by Roderick MacKinnon (Rockefeller University), who received the 2003 Nobel Prize in Chemistry for this work. The key K^+ ion–selecting portion of the channel is shown with side and top-down expansions using space-filling models of the $\text{C}=\text{O}$ groups that line the channel and blue potassium ions.



Drawings showing how the ion channel selectively allows K^+ ions through but not the smaller Na^+ cations. The K^+ on the left is large enough to interact equally well with all four square-planar O atoms that line the top part of the ion channel. Therefore, little energy is lost on dissociation of the coordinated water molecules (only four shown for clarity) as the K^+ ion enters the channel. Na^+ ions, however, are too small and can't interact well with all four of the O atoms lining the channel. This represents a higher energy situation and the Na^+ ion prefers to stay in the solution where it can interact with more water molecules.

amino acid oxygen atoms protruding from the channel walls. The distance between the bare K^+ ion and these oxygen atoms is similar to the distance between the K^+ and the oxygen atoms of its solvation shell. Thus, the potassium ion can shed its water shell and enter the rings with little energetic penalty (see the accompanying figure). In contrast, the smaller Na^+ ion cannot quite “reach” all of the oxygens in the channel's ring for bonding; the energetic barrier to desolvation is higher, and the Na^+ ion is excluded.

The human body is unquestionably the world's most sophisticated chemical reactor. It is amusing to contemplate our cells' crafty use of tools—molecular drinking straws and atomic tape measures—to keep our insides well stocked with nutritional staples.

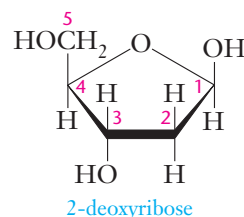
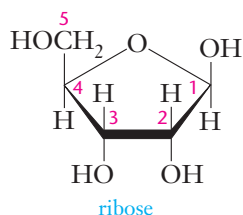
LISA SAUNDERS BAUGH

Unless otherwise noted, all content on this page is © Cengage Learning.



An idealized model of DNA.

George G. Stanley



The bases found in nucleic acids are shown in Figure 24-17. Each type of nucleic acid contains two pyrimidine bases and two purine bases. The two purine bases adenine (A) and guanine (G) and the pyrimidine base cytosine (C) are found in both RNA and DNA. In RNA, the other pyrimidine base is uracil (U), whereas DNA contains thymine (T). Specific pairs of these bases form hydrogen bonds to each other in specifically oriented arrangements, so they always occur in distinctive hydrogen-bonded base pairs. Adenine and thymine (in DNA) or uracil (in RNA) each form two hydrogen bonds, so they are always paired together; similarly, guanine and cytosine each form three hydrogen bonds, so they always pair to each other (Figure 24-18). The resulting complementary **base-pairing** links two strands of the polymer in a very specific order to form a double helix. This order is the key to nucleic acid function. Figure 24-19 shows a short segment of the double strand of DNA. In that figure, we see that adenine is paired with thymine and guanine is paired with cytosine. In RNA, adenine forms base pairs with uracil instead of with thymine.

DNA is one of the largest molecules known. Human DNA is estimated to have up to three billion base pairs, resulting in a molecular weight in the tens of billions. RNA is smaller and more variable, with molecular weights of 20,000 to 40,000. Genetic information for each organism is stored in its DNA as a result of the locations and sequence of the base pairs. The information is replicated when the strands unravel and new complementary strands are formed. The genetic information of the DNA is used to guide the many syntheses that occur in a living cell. For example, for the synthesis of a specific

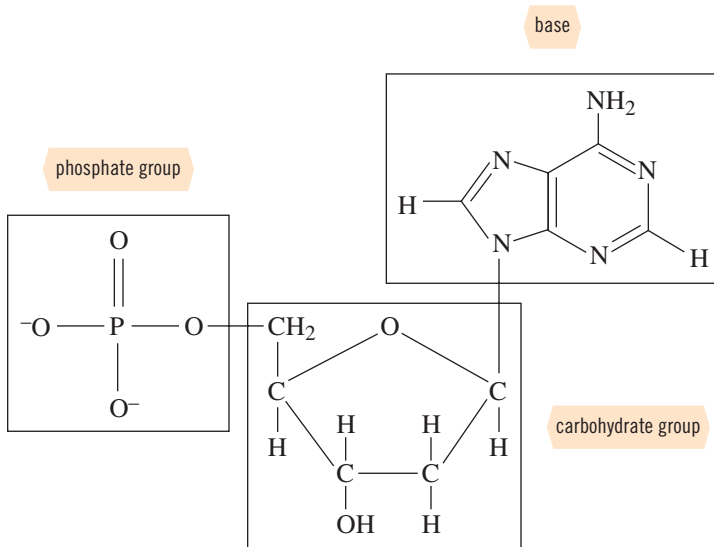


Figure 24-15 The three kinds of units that are polymerized to form nucleic acids.

Unless otherwise noted, all content on this page is © Cengage Learning.

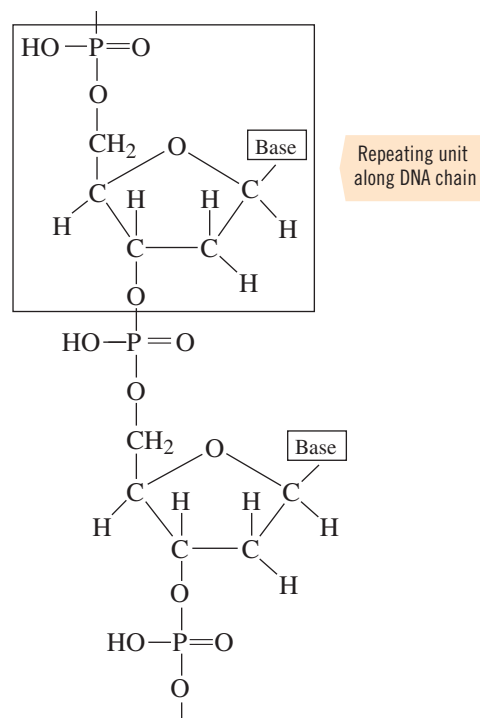


Figure 24-16 A short segment of DNA (deoxyribonucleic acid).

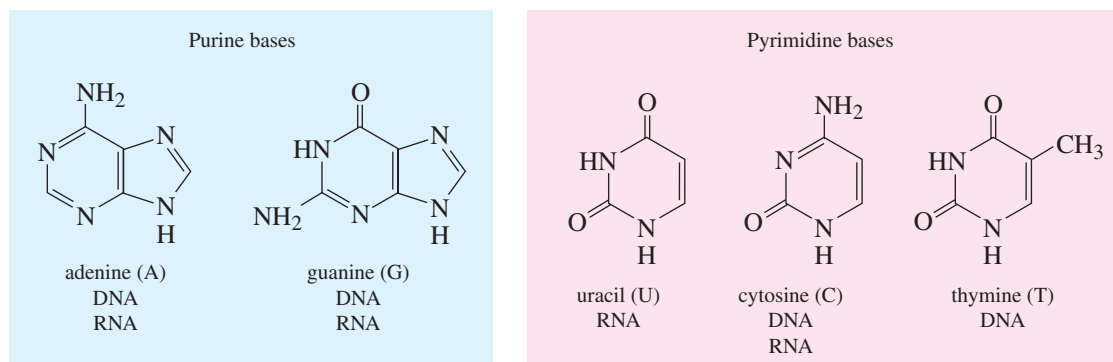


Figure 24-17 The bases found in DNA and RNA.

protein, a specific portion of the DNA double helix unwinds. Then an RNA molecule is built using the sequence of base pairs of the DNA as a pattern. The RNA then migrates from the cell's nucleus to the location where the protein is to be synthesized. There the base sequence of the RNA determines the sequence of amino acids to be used in the protein construction. With its many possible sequences of the same base pairs to transmit information to control synthesis of other molecules, DNA contains a vast amount of genetic information.

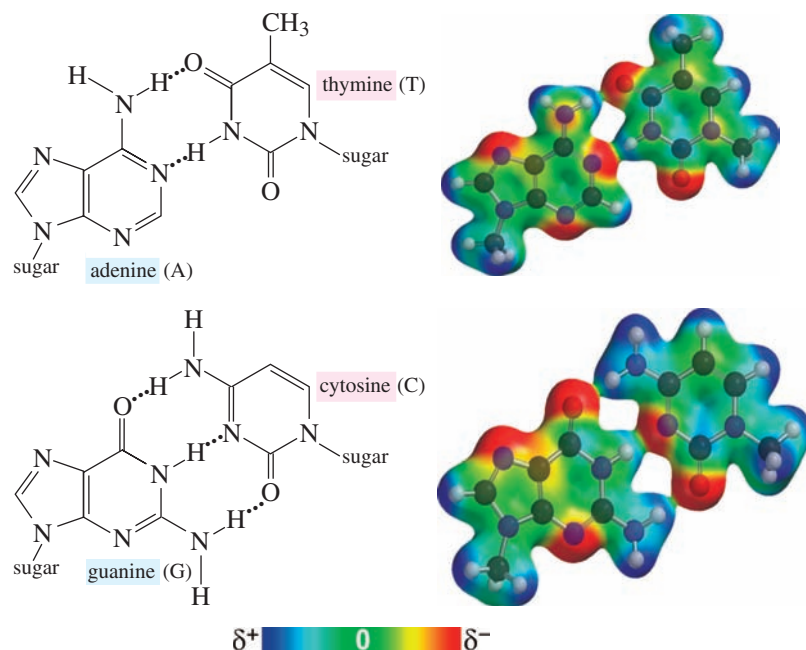


Figure 24-18 The two kinds of hydrogen-bonded base-pairing that occur in DNA. In RNA, adenine forms a base pair with uracil instead of with thymine.

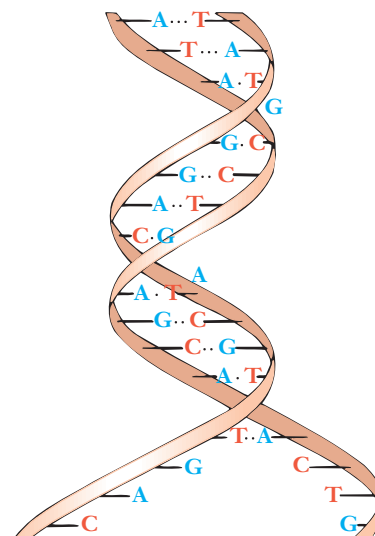


Figure 24-19 A short segment of the double strand of a DNA molecule.

KEY TERMS

Achiral Describes an object that *can* be superimposed with its mirror image.

Aldose A monosaccharide that contains an aldehyde group.

Base-pairing The complementary hydrogen bonding of cytosine with guanine and of adenine with thymine (in DNA) or with uracil (in RNA).

Biopolymer Polymers found in biological systems.

Bronsted-Lowry acid A species that acts as a proton donor.

Bronsted-Lowry base A species that acts as a proton acceptor.

Carbohydrate A biopolymer made up of saccharide units.

Chiral Describes an object that *cannot* be superimposed with its mirror image.

Conformation One specific geometry of a molecule. The conformations of a compound differ from one another only by rotation about single bonds.

Constitutional isomers Compounds that contain the same number of the same kinds of atoms but that differ in the order in which their atoms are bonded together; also known as *structural isomers*.

2-Deoxyribose The carbohydrate found in DNA.

Dipeptide A compound in which two amino acid monomers have joined to form the peptide.

Disaccharide A molecule consisting of two monosaccharides joined together by a glycosidic bond.

DNA Deoxyribonucleic acid; a nucleic acid consisting of phosphate, 2-deoxyribose, and the four bases adenine, cytosine, guanine, and thymine.

Enantiomers See *Optical isomers*.

Enzyme A protein that catalyzes a biological reaction.

Geometric isomers Compounds with different arrangements of groups on the opposite sides of a bond with restricted rotation, such as a double bond or a single bond in a ring; for example, *cis-trans* isomers of certain alkenes.

Glycosidic bond A bond linking monomers in a polysaccharide.

Heat of combustion The amount of energy *liberated* per mole of substance burned.

Ketose A monosaccharide that contains a ketone group.

Monomers The small molecules from which polymers are formed.

Monosaccharide Simple sugars (monomers) from which more complex carbohydrates are constructed.

Nucleic acid A biopolymer consisting of repeating units of ribose or deoxyribose, phosphate, and selected bases.

Oligosaccharide A molecule consisting of four to ten monosaccharides joined together by glycosidic bonds.

Optical activity The rotation of a plane of polarized light by chiral molecules.

Optical isomers Molecules that are nonsuperimposable mirror images of each other, that is, that bear the same relationship to each other as do left and right hands; also known as *enantiomers*.

Oxidation (as applied to organic compounds) The increase of oxygen content or the decrease of hydrogen content of an organic molecule.

Peptide bond A bond formed by elimination of a molecule of water between the amino group of one amino acid and the carboxylic acid group of another.

Peptides Compounds formed by the linking of small numbers of amino acids.

Polymerization The combination of many small molecules (monomers) to form large molecules (polymers).

Polymers Large molecules formed by the combination of many small molecules (monomers).

Polypeptide A polymer composed of amino acids linked by peptide bonds.

Polysaccharide Carbohydrates that contain more than ten monosaccharide units.

Primary structure The sequence of the monomeric units in proteins, carbohydrates, and so on.

Protein A naturally occurring polymeric chain of L-amino acids linked together by peptide bonds.

Racemic mixture A single sample containing equal amounts of the two enantiomers (optical isomers) of a compound; does not rotate the plane of polarized light.

Reduction (as applied to organic compounds) The decrease of oxygen content or the increase of hydrogen content of an organic molecule.

Ribose The carbohydrate found in RNA.

RNA Ribonucleic acid; a nucleic acid consisting of phosphate, ribose, and the four bases adenine, cytosine, guanine, and uracil.

Saponification The hydrolysis of esters in the presence of strong bases.

Soap The alkali metal (Na or K) salt of a long-chain fatty acid.

Stereochemistry The study of the three-dimensional aspects of molecular structures.

Stereoisomers Isomers in which the atoms are linked together in the same atom-to-atom order, but with different arrangements in space. See *Geometric isomers*; *Optical isomers*.

Trisaccharide A molecule consisting of three monosaccharides joined together by glycosidic bonds.

EXERCISES

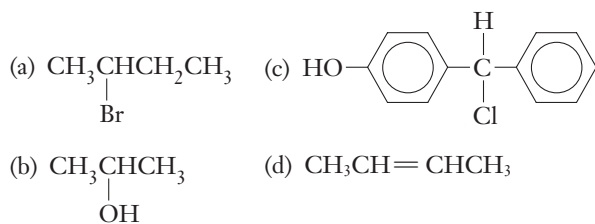
● Molecular Reasoning exercises

▲ More Challenging exercises

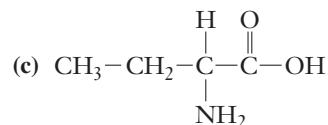
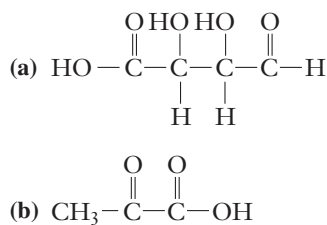
Blue-Numbered exercises are solved in the Student Solutions Manual

Geometries of Organic Molecules

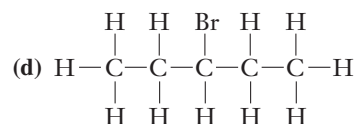
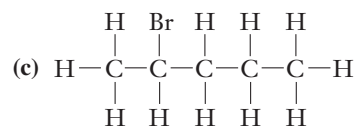
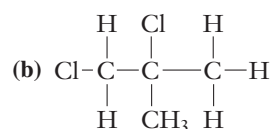
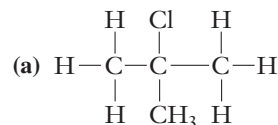
- Distinguish between two types of constitutional isomerism. Give an example of each type.
- Distinguish between two types of stereoisomerism. Give an example of each type.
- Which of the following compounds can exist as *cis* and *trans* isomers? Draw and label them.
(a) 2,3-dimethyl-2-butene; (b) 2-chloro-2-butene;
(c) dichlorobenzene; (d) 1,1-dichlorocyclobutane
- Which of the following compounds can exist as *cis* and *trans* isomers? Draw and label them. (a) 2-butene;
(b) 1,2-dibromo-2-butene; (c) 2-bromo-2-butene;
(d) 1,2-dichlorocyclopentane
- Write formulas and names for the isomers of
(a) bromochlorobenzene, (b) trifluorobenzene, and
(c) chlorotoluene. What kind of isomerism is illustrated by each of these sets of compounds?
- Write formulas and names for the isomers of
(a) butanol, (b) pentachloropropene, and
(c) chlorofluoroethane.
- Distinguish between conformations and isomers.
- Draw structural representations of two conformations of cyclohexane. Give the name commonly applied to each.
- Draw structural representations of two conformations of butane. Indicate the one having the lower potential energy.
- What is optical isomerism? What are enantiomers?
- Which of the following compounds would exhibit optical isomerism?



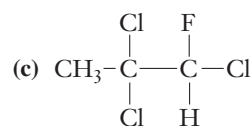
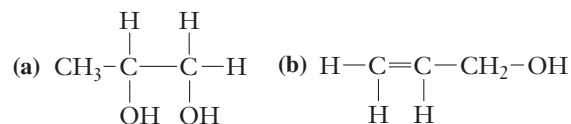
- Draw three-dimensional representations of the enantiomeric pairs in Exercise 11.
- Circle the chiral centers, if any, in these molecules.



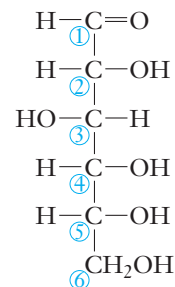
- Circle the chiral centers, if any, in these compounds.



- Locate the chiral carbon(s), if any, in the following molecules.



- A formula may represent more than two stereoisomers if it has more than one asymmetric carbon atom. The number of stereoisomers doubles for each additional asymmetric carbon atom. The monosaccharide glucose can be represented by the structural formula to the right. How many asymmetric carbon atoms does a glucose molecule have? How many stereoisomers of this general structure are there?



● Molecular Reasoning exercises

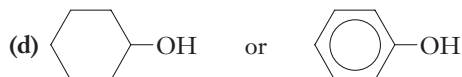
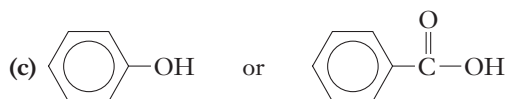
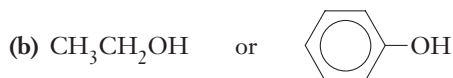
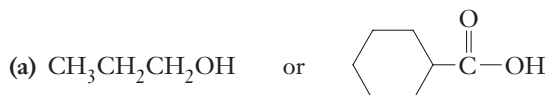
▲ More Challenging exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

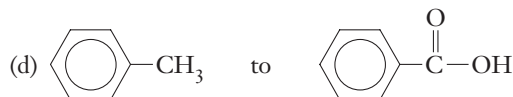
Selected Reactions

17. (a) List the four most acidic organic functional groups. (b) List the four common organic functional groups that are bases. (c) Which common organic base contains a benzene ring?
18. Why are aqueous solutions of amines basic? Show, with equations, how the dissolution of an amine in water is similar to the dissolution of ammonia in water.
19. Show that the reactions of amines with inorganic acids such as HCl are similar to the reactions of ammonia with inorganic acids.
20. What are the equilibrium concentrations of the species present in a 0.12 M solution of aniline? $K_b = 4.2 \times 10^{-10}$
- $$\text{C}_6\text{H}_5\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$$
21. Which solution would be more acidic: a 0.12 M solution of aniline hydrochloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ ($K_b = 4.2 \times 10^{-10}$ for aniline, $\text{C}_6\text{H}_5\text{NH}_2$), or a 0.12 M solution of methylamine hydrochloride, $\text{CH}_3\text{NH}_3\text{Cl}$ ($K_b = 5.0 \times 10^{-4}$ for methylamine, CH_3NH_2)? Justify your choice.
22. Choose the compound that is the stronger acid in each set.



23. Draw the structures of the first two oxidation products of each of these alcohols.
(a) $\text{CH}_3\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
24. What product could be produced by the mild oxidation of 2-propanol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$?
- $$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ | \\ \text{OH} \end{array}$$
25. (a) What are alkoxides? (b) What do we mean when we say that the alkoxides are strong bases?
26. (a) Write equations for the reactions of three alcohols with metallic sodium. (b) Name all compounds in these equations. (c) Show how these reactions are similar to the reaction of metallic sodium with water.

27. Which physical property of aldehydes is used to advantage in their production from alcohols?
28. The K_b for Lidocaine (a monobasic organic compound, MW = 234.3) is 7.0×10^{-6} . What is the pH of a 1.2 percent solution of Lidocaine? The density of the solution is 1.00 g/mL.
29. How are the terms "oxidation" and "reduction" often used in organic chemistry? Classify the following changes as either oxidation or reduction:
(a) CH_4 to CH_3OH ; (b) $\text{CH}_2=\text{CH}_2$ to CH_3-CH_3 ;
(c) $\text{CH}_3\text{CH}_2\text{CHO}$ to $\text{CH}_3\text{CH}_2\text{CH}_3$;



30. Classify the following changes as either oxidation or reduction: (a) CH_3OH to CO_2 and H_2O ; (b) CH_2CH_2 to CH_3CHO ; (c) CH_3COOH to CH_3CHO ; (d) $\text{CH}_3\text{CH}_2=\text{CH}_2$ to $\text{CH}_3\text{CH}_2\text{CH}_3$.
31. Describe the preparation of three aldehydes from alcohols, and write appropriate equations. Name all reactants and products.
32. Describe the preparation of three ketones from alcohols, and write appropriate equations. Name all reactants and products.
33. Write equations to illustrate the oxidation of the following aromatic hydrocarbons by potassium permanganate in basic solution: (a) toluene; (b) ethylbenzene; (c) 1,2-dimethylbenzene.
34. (a) Do you expect toluene to produce soot as it burns? Why? (b) Would you expect the flame to be blue or yellow?
35. An ester is the product of the reaction of an alcohol with a carboxylic acid and is the organic version of an inorganic salt. What is an inorganic ester?
36. (a) Write equations for the formation of three inorganic esters. (b) Name the inorganic ester formed in each case.
37. (a) What is nitroglycerine? (b) Write the chemical equation that shows the preparation of nitroglycerine. (c) List two important uses for nitroglycerine. Are they similar?
38. Write equations for the formation of three different esters, starting with an acid and an alcohol in each case. Name all compounds.
39. Write equations for the formation of three different esters, starting with a different acid chloride and a different alcohol in each case. Name all compounds.
40. Write equations for the hydrolysis of (a) butyl acetate, (b) ethyl formate, (c) methyl acetate, and (d) octyl acetate. Name all products.
41. (a) What is a saponification reaction? (b) Why is this kind of reaction called saponification?

Biopolymers

42. What is necessary if a molecule is to be capable of polymerization? Name three types of molecules that can polymerize.



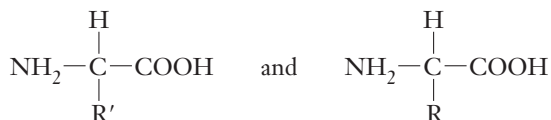
Charles D. Winters

Cellulose acetate products

43. A cellulose polymer has a molecular weight of 750,000. Estimate the number of units of the monomer, α -glucose ($C_6H_{12}O_6$) in this polymer. This polymerization reaction can be represented as



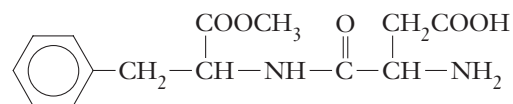
44. Write structural formulas of two monosaccharides that contain six carbon atoms.
45. Write the structural formula of a trisaccharide containing only α -1,4-linked glucose units.
46. Write two structural formulas of fructose, one in its cyclic form and one in its straight-chain form.
47. What functional groups are found in carbohydrate molecules?
48. A dipeptide has two structural isomers. For example, combining glycine and alanine produces both Gly-Ala and Ala-Gly. A tripeptide has six structural isomers. For example, combining glycine, alanine and valine produces Gly-Ala-Val, Gly-Val-Ala, Ala-Gly-Val, Ala-Val-Gly, Val-Gly-Ala and Val-Ala-Gly. How many structural isomers does a tetrapeptide made from 4 different amino acids have?
49. Describe the structure of a natural amino acid molecule. What kind of isomerism do most amino acids exhibit? Why?
50. How are the amino acid units in a polypeptide joined together? What are the links called?
51. Consider the following two amino acids:



Write the structural formulas for the dipeptides that could be formed containing one molecule of each amino acid.

52. How many different dipeptides can be formed from the three amino acids A, B, and C? Write the sequence of amino acids in each. Assume that an amino acid could occur more than once in each dipeptide.

53. How many different tripeptides can be formed from the two amino acids A and B? Write the sequence of amino acids in each. Assume that an amino acid can occur no more than twice in each tripeptide.
54. Aspartame (trade name NutraSweet) is a methyl ester of a dipeptide:



Write the structural formulas of the two amino acids that are combined to make aspartame (ignoring optical isomerism).



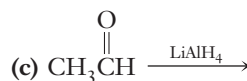
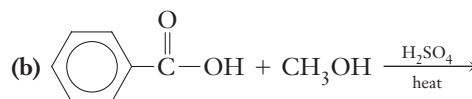
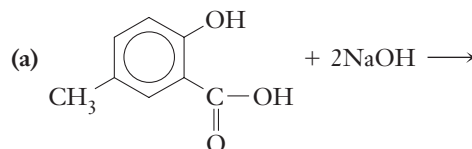
Charles D. Winters

Equal

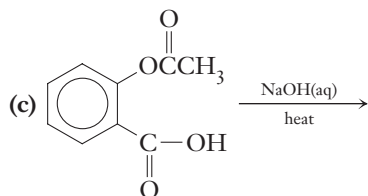
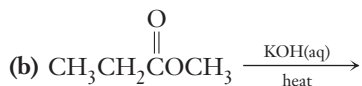
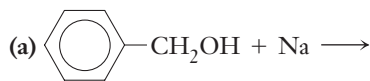
55. Write the structural formula of the carbohydrate found in deoxyribonucleic acid (DNA). How does this carbohydrate differ from the one found in ribonucleic acid (RNA)?
56. Write structural formulas of the four bases found in DNA. Circle at least one functional group on each that gives the compound its base properties.
57. Draw a short segment of the DNA biopolymer that contains three each of the phosphate, carbohydrate, and base groups.
58. In the double-strand form of DNA, the base groups are paired. What base is found paired (hydrogen bonded) with thymine?

Mixed Exercises

59. Identify the major products of each reaction.



60. Identify the major products of each reaction.



61. Write a structural formula for each of the following compounds:
 (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (d) CH_3OCH_3
 (b) CH_3COOH (e) $\text{CH}_3\text{CHCH}_2\text{CH}_3$
 (c) $\text{CH}_3\text{CHOHCH}_3$
62. Write a structural formula for each of the following compounds:
 (a) $\text{CH}_3\text{CH}_2\text{ONO}_2$ (d) $\text{ClCH}_2\text{CClCHCl}$
 (b) CH_3CHCH_2 (e) $\text{CH}_3\text{CH}_2\text{CH}_2\text{ONa}$
 (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
63. (a) Name three biopolymers found in animals. (b) Name at least one biopolymer that is composed of identical monomers.
64. Name the three types of monomers that are found in DNA. Give a structural formula for an example of each.

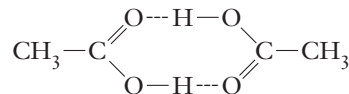
Conceptual Exercises

65. Nylon is decomposed by acids, but polyethylene is not. Suggest an explanation for this difference in behavior.
66. How does the heat of combustion of ethyl alcohol compare with the heats of combustion of low-molecular-weight saturated hydrocarbons on a per-mole basis and on a per-gram basis?
67. What type of alcohol cannot be oxidized by mild oxidation? Why not?
68. Examine the heats of combustion in Table 24-3. Why is the heat of combustion for ethanol, in J/g, so much less than those for the alkanes?
69. What holds the two intertwined polynucleotide chains of the DNA double helix together?
70. Within the human body, DNA most directly controls the formation of which group of biochemical compounds?

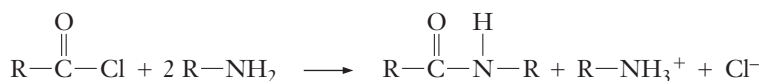
Building Your Knowledge

71. (a) In aqueous solution, acetic acid exists mainly in the molecular form ($K_a = 1.8 \times 10^{-5}$). Calculate the freezing point depression for a 0.10 molal aqueous solution of acetic

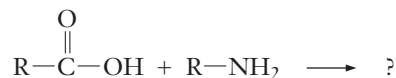
acid, ignoring any ionization of the acid. $K_f = 1.86^\circ\text{C/molal}$ for water. (b) In nonpolar solvents such as benzene, acetic acid exists mainly as dimers as a result of hydrogen bonding. Calculate the freezing point depression for a 0.10 molal solution of acetic acid in benzene. $K_f = 5.12^\circ\text{C/molal}$ for benzene. Assume complete dimer formation.



72. What is the pH of a 0.12 M solution of sodium benzoate? $K_a = 6.3 \times 10^{-5}$ for benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$. Would this solution be more or less acidic than a 0.12 M solution of sodium acetate? $K_a = 1.8 \times 10^{-5}$ for acetic acid, CH_3COOH .
73. (a) A sample of an organic compound contains only carbon, hydrogen, and oxygen. Combustion of a 0.240 g sample of this compound produces 0.352 g of carbon dioxide and 0.144 g of water. What is the simplest formula of the compound? (b) A solution containing 0.20 g of the compound dissolved in 25.0 g of water freezes at -0.248°C . What is the molecular formula of the compound?
74. Acetic acid (CH_3COOH) is a weak acid ($K_a = 1.8 \times 10^{-5}$). Replacing one or more of the methyl hydrogen atoms with chlorine atoms increases the acidity: monochloroacetic acid (ClCH_2COOH), $K_a = 1.5 \times 10^{-3}$; dichloroacetic acid (Cl_2CHCOOH), $K_a = 5.0 \times 10^{-2}$; trichloroacetic acid (Cl_3CCOOH), $K_a = 2.0 \times 10^{-1}$. Why does the presence of one or more chlorine atoms increase the strength of acid?
75. Amides are often prepared by the reaction of an acyl halide with ammonia, a primary amine, or a secondary amine:

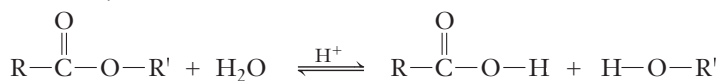


What type of product would be obtained if the carboxylic acid were combined with the nitrogen compound:

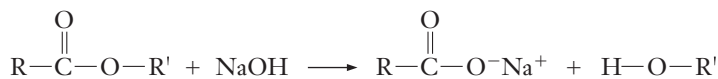


76. Hydrolysis of esters can be either acid-catalyzed or base-catalyzed (saponification)

acid-catalyzed:



base-catalyzed:



What significant difference between these two reactions results in a preference for use of the base-catalyzed reaction?

Beyond the Textbook

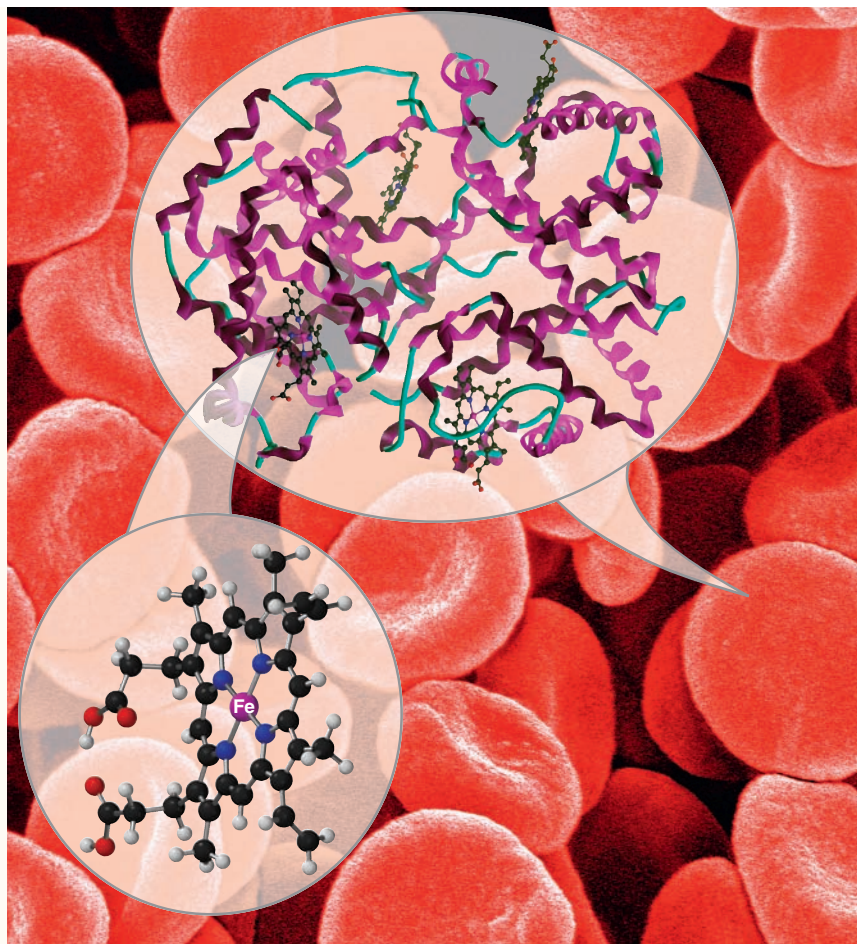
NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.*

77. In a science reference book such as *The Merck Index*, locate the descriptions of sorbose, fructose, and glucose. Answer the following questions. (Note: You may need assistance from your instructor to locate copies of *The Merck Index*.) (a) Which of the three compounds is sweetest? (b) Large quantities of sorbose are used to produce large quantities of what compound?
78. Open www.moleday.org or another website and answer the following: (a) When is Mole Day celebrated? (b) Select your favorite organic mole joke.
79. Open www.dnaftb.org or another website and locate answers to the following questions. (a) What part did Rosalind E. Franklin play in the determination of the structure of DNA? (b) Why was she not awarded a share in the Nobel Prize?



Coordination Compounds

25



Red blood cells (1300x). The red blood cells that transport O_2 throughout our bodies contain hemoglobin, a protein. Each hemoglobin molecule contains four heme groups, each consisting of one Fe^{2+} ion coordinated to a porphyrin molecule.

© Corbis

OUTLINE

25-1 Coordination Compounds

25-2 Ammine Complexes

25-3 Important Terms

25-4 Nomenclature

25-5 Structures

Isomerism in Coordination Compounds

25-6 Structural (Constitutional) Isomers

25-7 Stereoisomers

Bonding in Coordination Compounds

25-8 Crystal Field Theory

25-9 Color and the Spectrochemical Series

OBJECTIVES

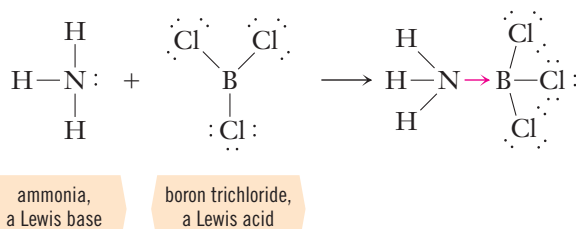
After you have studied this chapter, you should be able to

- ▶ Recognize coordination compounds
- ▶ Recognize metals that form soluble ammine complexes in aqueous solutions and write the formulas for common ammine complexes
- ▶ Use the terminology that describes coordination compounds
- ▶ Apply the rules for naming coordination compounds
- ▶ Recognize common structures of coordination compounds
- ▶ Describe various kinds of structural (constitutional) isomerism and distinguish among structural isomers
- ▶ Recognize stereoisomers
- ▶ Describe the crystal field theory of bonding in coordination compounds
- ▶ Explain the origin of color in complex species
- ▶ Use the spectrochemical series to explain colors of a series of complexes

Coordination compounds are found in many places on the earth's surface. Every living system includes many coordination compounds. They are also important components of everyday products as varied as cleaning materials, medicines, inks, and paints. A list of important coordination compounds appears to be endless because many new ones are discovered every year.

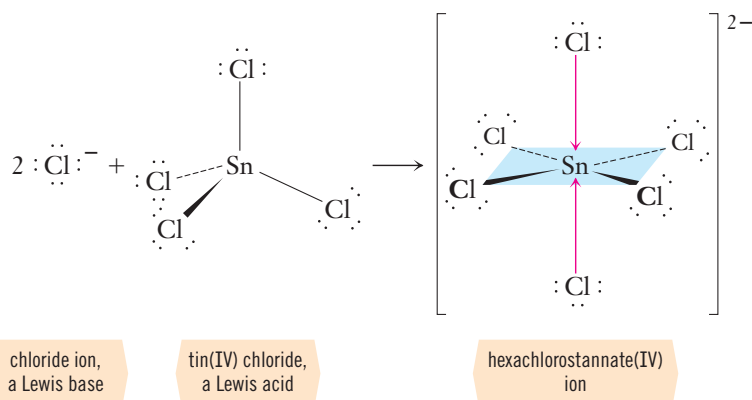
25-1 Coordination Compounds

In Section 10-10, we discussed the Lewis acid–base concept. A *base* makes available a share in an electron pair, and an *acid* accepts a share in an electron pair to form a **coordinate covalent bond** or **dative bond**. To emphasize this type of bonding, we sometimes represent the dative bonds by arrows that point from the electron pair donor (Lewis base) to the acceptor (Lewis acid). But we usually just draw straight lines (or wedges or dashed lines) to indicate a bond.



▶ Covalent bonds in which the shared electron pair is provided by one atom are called *coordinate covalent* or *dative bonds*.

▶ The red arrows represent dative bonds. These arrows do not imply that two of the Sn — Cl bonds are different from the others. Once formed, the Sn — Cl bonds in the [SnCl₆]^{2−} ion are all alike.



Common oxidation states and *d*-electron counts for the transition metals are given in Table 25-1. Most *d*-transition metal ions have vacant *d* orbitals that can accept shares in electron pairs. Most act as Lewis acids by forming dative bonds with Lewis bases that donate one or more lone pairs of electrons in **coordination compounds (coordination com-**

plexes, or complex ions). The Lewis bases that bond to metal atoms or ions are called **ligands**. Complexes of transition metal ions or molecules include cationic species (e.g., $[\text{Cr}(\text{OH}_2)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Ag}(\text{NH}_3)_2]^+$), anionic species (e.g., $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{MnCl}_3]^{3-}$), and neutral species (e.g., $[\text{Fe}(\text{CO})_5]$, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$). Many complexes are very stable, as indicated by their low dissociation constants, K_d (see Section 20-6 and Appendix I).

Many important biological substances contain coordinated metal atoms or ions. Hemoglobin and chlorophyll are two examples (Figure 25-1). Hemoglobin is a protein that carries O_2 in blood. It contains iron(II) ions bound to large porphyrin rings. The transport of oxygen by hemoglobin involves the coordination and subsequent release of O_2 molecules by the Fe(II) ions. Chlorophyll is necessary for photosynthesis in plants. It contains magnesium ions bound to porphyrin rings. Vitamin B_{12} is a large complex of cobalt. Coordination compounds have many important applications in such areas as medicine, water treatment, soil and plant treatment, protection of metal surfaces, analysis of trace amounts of metals, electroplating, catalysis, and textile dyeing.

► We often write water as OH_2 rather than H_2O when we want to emphasize that the water is bonded to the metal through oxygen, the donor atom.

Table 25-1 Common Oxidation States and d -Electron Counts for the Transition Metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3 d^0	+3 d^1 +4 d^0	+3 d^2 +5 d^0	0 d^6 +2 d^4 +3 d^3 +4 d^2 +6 d^0	+1 d^6 +2 d^5 +3 d^4 +5 d^2 +7 d^0	0 d^8 +2 d^6 +3 d^5	0 d^9 +1 d^8 +2 d^7 +3 d^6	0 d^{10} +2 d^8	+1 d^{10} +2 d^9	+2 d^{10}
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3 d^0	+4 d^0	+3 d^2 +5 d^0	0 d^6 +2 d^4 +4 d^2 +6 d^0	+1 d^6 +3 d^4 +5 d^2 +7 d^0	0 d^8 +2 d^6 +3 d^5	0 d^9 +1 d^8 +2 d^7 +3 d^6	0 d^{10} +2 d^8 +4 d^6	+1 d^{10}	+2 d^{10}
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3 d^0	+4 d^0	+3 d^2 +5 d^0	0 d^6 +2 d^4 +4 d^2 +6 d^0	+1 d^6 +2 d^5 +3 d^4 +5 d^2 +7 d^0	0 d^8 +2 d^6 +3 d^5	0 d^9 +1 d^8 +2 d^7 +3 d^6	0 d^{10} +2 d^8 +4 d^6	+1 d^{10} +2 d^9 +3 d^8	+2 d^{10}

► When Lewis bases bond to a transition metal, the d orbitals always fill before the next higher s orbital. The filled noble gas electron configuration associated with each transition metal is usually omitted and just the valence d -electron count is shown.

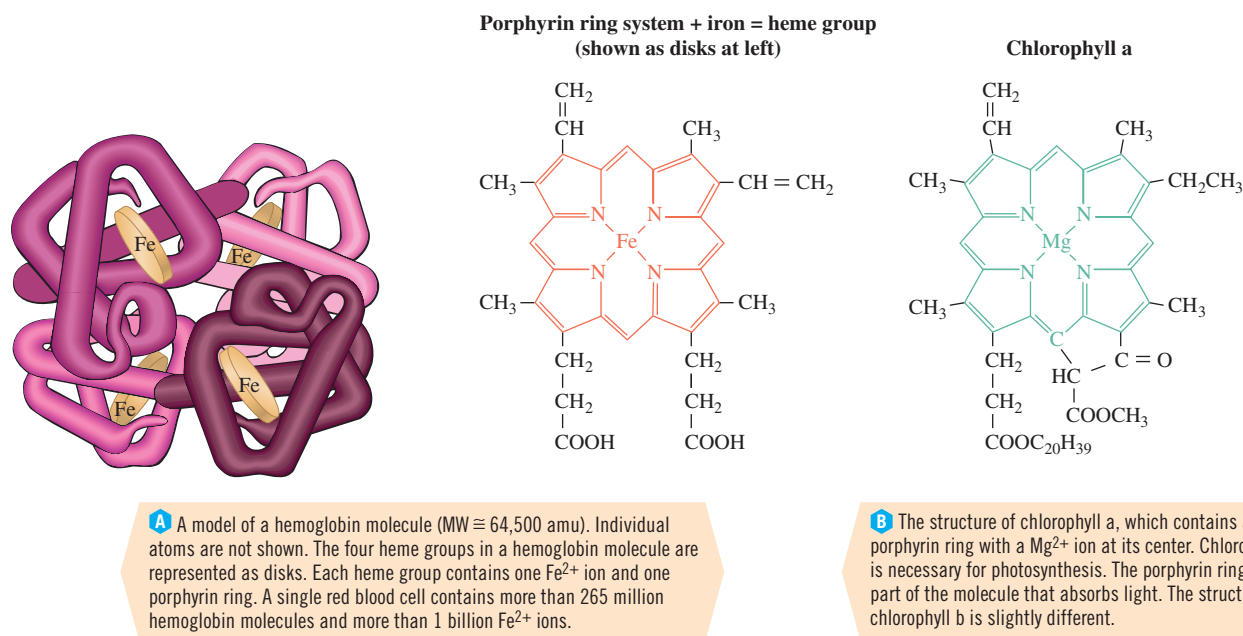


Figure 25-1 Hemoglobin and some metalloporphyrin structures.

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 25-2 Interpretation of Experimental Data by Werner

Formula	Equivalents of AgCl Precipitated per Formula Unit	Number of Ions per Formula Unit (based on conductance)	True Formula	Ions/Formula Unit
PtCl ₄ · 6NH ₃	4	5	[Pt(NH ₃) ₆]Cl ₄	[Pt(NH ₃) ₆] ⁴⁺ 4 Cl ⁻
PtCl ₄ · 5NH ₃	3	4	[Pt(NH ₃) ₅ Cl]Cl ₃	[Pt(NH ₃) ₅ Cl] ³⁺ 3 Cl ⁻
PtCl ₄ · 4NH ₃	2	3	[Pt(NH ₃) ₄ Cl ₂]Cl ₂	[Pt(NH ₃) ₄ Cl ₂] ²⁺ 2 Cl ⁻
PtCl ₄ · 3NH ₃	1	2	[Pt(NH ₃) ₃ Cl ₃]Cl	[Pt(NH ₃) ₃ Cl ₃] ⁺ Cl ⁻
PtCl ₄ · 2NH ₃	0	0	[Pt(NH ₃) ₂ Cl ₄]	no ions

► Double salts are ionic solids resulting from the cocrystallization of two salts from the same solution into a single structure. In the example given in the text, the solid is produced from an aqueous solution of iron(II) sulfate, FeSO₄, and ammonium sulfate, (NH₄)₂SO₄.

► The conductance of a solution of an electrolyte is a measure of its ability to conduct electricity. It is related to the number of ions and the charges on ions in solution.

Bonding in transition metal complexes was not understood until the pioneering research of Alfred Werner (1866–1919), a Swiss chemist who received the Nobel Prize in chemistry in 1913. Great advances have been made since in the field of coordination chemistry, but Werner's work remains the most important contribution by a single researcher.

Prior to Werner's work, the formulas of transition metal complexes were written with dots (e.g., CrCl₃ · 6H₂O, AgCl · 2NH₃) just like double salts such as iron(II) ammonium sulfate hexahydrate (FeSO₄ · (NH₄)₂SO₄ · 6H₂O). The properties of solutions of double salts are the properties expected for solutions made by mixing the individual salts. However, a solution of AgCl · 2NH₃, or more properly [Ag(NH₃)₂]Cl, behaves quite differently from either a solution of (very insoluble) silver chloride or a solution of ammonia. The dots have been called “dots of ignorance” because they signified that the mode of bonding was unknown. Even today, many common coordination compounds, such as CrCl₃ · 6H₂O, are still written this way even though the most common coordination formula in the solid state is [CrCl₂(OH₂)₄]Cl · 2H₂O. When this complex is dissolved in water, [CrCl(OH₂)₅]²⁺ and eventually [Cr(OH₂)₆]³⁺ are formed by chloride ligand dissociation and replacement with water molecules. Table 25-2 summarizes the types of experiments Werner performed and interpreted to lay the foundations for modern coordination theory.

Werner isolated platinum(IV) compounds with the formulas that appear in the first column of Table 25-2. He added excess AgNO₃ to solutions of carefully weighed amounts of the five salts. The precipitated AgCl was collected by filtration, dried, and weighed. He determined the number of moles of AgCl produced. This told him the number of moles of Cl⁻ ions precipitated per mole of Pt compound (second column of Table 25-2). Werner reasoned that the precipitated Cl⁻ ions must be free (uncoordinated), whereas the unprecipitated Cl⁻ ions must be bonded to Pt so they could not be precipitated by Ag⁺ ions. He also measured the conductances of solutions of these compounds of known concentrations. By comparing these with data on solutions of simple electrolytes, he found the number of chloride ions per formula unit. The results are shown in the third column. Piecing the evidence together, he concluded that the correct formulas are the ones listed in the last two columns. The NH₃ and Cl⁻ within the brackets are bonded by dative bonds to the Lewis acid, the Pt(IV) ion.

Charles D. Winters



Crystals of copper(II) sulfate pentahydrate. This hydrate, usually written as CuSO₄ · 5H₂O, is more properly shown by the coordination formula, [Cu(OH₂)₄(SO₄)] · H₂O. The solid-state structure has four water molecules that are coordinated to the Cu²⁺ ion in a square planar arrangement, with two very weakly bonded SO₄²⁻ anions that bridge between different [Cu(OH₂)₄]²⁺ complexes. The other water molecule is held in the solid by hydrogen bonding.

Unless otherwise noted, all content on this page is © Cengage Learning.

The charge on a complex is the sum of the oxidation state of the metal center and the charges on the ligands.

We can use this relationship to determine or confirm the charge on a complex species. For example, the charge on [Pt(NH₃)₆]⁴⁺ can be calculated as

$$\begin{aligned}\text{Charge} &= [\text{charge on Pt(IV)}] + 6 \times (\text{charge on NH}_3) \\ &= (4+) + 6 \times (0) = 4+\end{aligned}$$

The charge on $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$ is

$$\begin{aligned}\text{Charge} &= [\text{charge on Pt(IV)}] + 4 \times (\text{charge on NH}_3) + 2 \times (\text{charge on Cl}^-) \\ &= (4+) + 4 \times (0) + 2 \times (1-) = 2+\end{aligned}$$

The oxidation state of the transition metal is very important and is indicated in a variety of ways. The formal notation is to use a Roman numeral in parentheses after the element symbol, as in Pt(IV). But the oxidation state can also be shown in the following ways, which are all equivalent and commonly used: Pt(+4), Pt^{4+} , and Pt^{IV} . The oxidation state of an atom is indicated whenever a metal atom appears by itself with a charge (Cu^{2+} , Rh^0 , Co^{1+}). In order to figure out the oxidation state of a transition metal in a coordination complex, one must know the charges on the ligands (usually neutral or anionic) and the overall charge on the complex without any counterions present (or the charge on the counterion if present). You can practice this technique by verifying that the Pt atoms in Table 25-2 are all in the +4 oxidation state.



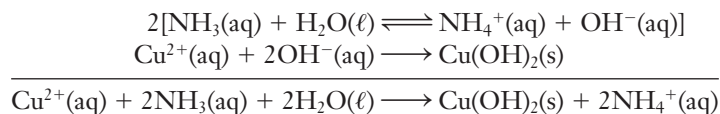
Charles D. Winters

Colors of coordination compounds depend on which metals and ligands are present. From left: the $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ion is purple; the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ion is green; the $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ion is light blue; and the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion is deep blue.

25-2 Ammine Complexes

Ammine complexes contain NH_3 molecules bonded to metal ions. Because the ammine complexes are important compounds, we will describe some of them briefly.

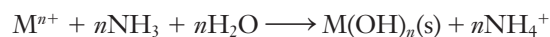
Most metal hydroxides are insoluble in water, so aqueous NH_3 initially reacts with nearly all metal ions to form insoluble metal hydroxides, or hydrated oxides.



Similarly,



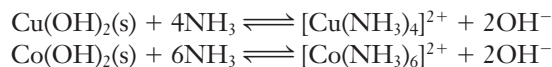
In general terms, we can represent this reaction as



where M^{n+} represents all of the common metal ions *except* the cations of the strong bases (Group 1A cations and the heavier members of Group 2A: Ca^{2+} , Sr^{2+} , and Ba^{2+}).

The hydroxides of some metals and some metalloids are amphoteric (see Section 10-6). Aqueous NH_3 is a weak base ($K_b = 1.8 \times 10^{-5}$), so the $[\text{OH}^-]$ in an ammonia solution is too low to dissolve amphoteric hydroxides by forming hydroxo complexes.

A number of metal hydroxides do dissolve, however, in an excess of aqueous NH_3 to form ammine complexes. For example, the hydroxides of copper and cobalt are readily soluble in an excess of *aqueous* ammonia solution. This occurs because of the reaction of NH_3 (a relatively good ligand) with the metal atoms to produce charged ammine complexes.

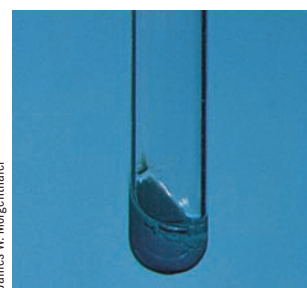


Interestingly, the metal hydroxides that exhibit this behavior are derived from the 12 metals of the cobalt, nickel, copper, and zinc families. All the common cations of these metals except Hg_2^{2+} (which disproportionates) form soluble complexes in the presence of excess aqueous ammonia (Table 25-3).



Charles D. Winters

The careful addition of aqueous NH_3 to the top of a light blue solution of Cu^{2+} ions (*bottom of beaker*) produces a grayish-white $\text{Cu}(\text{OH})_2$ precipitate (*middle*) and the soluble dark blue tetraammine complex, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (*top*).



James W. Mortenthaler



James W. Mortenthaler

$\text{Co}(\text{OH})_2$ (a blue compound that turns gray quickly) dissolves in excess aqueous NH_3 to form $[\text{Co}(\text{NH}_3)_6]^{2+}$ ions (*yellow-orange*).

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 25-3 Common Metal Ions That Form Soluble Complexes with an Excess of Aqueous Ammonia^a

Metal Ion	Insoluble Hydroxide Formed by Limited Aq. NH ₃	Complex Ion Formed by Excess Aq. NH ₃
Co ²⁺	Co(OH) ₂	[Co(NH ₃) ₆] ²⁺
Co ³⁺	Co(OH) ₃	[Co(NH ₃) ₆] ³⁺
Ni ²⁺	Ni(OH) ₂	[Ni(NH ₃) ₆] ²⁺
Cu ⁺	CuOH $\longrightarrow \frac{1}{2}$ Cu ₂ O ^b	[Cu(NH ₃) ₂] ⁺
Cu ²⁺	Cu(OH) ₂	[Cu(NH ₃) ₄] ²⁺
Ag ⁺	AgOH $\longrightarrow \frac{1}{2}$ Ag ₂ O ^b	[Ag(NH ₃) ₂] ⁺
Zn ²⁺	Zn(OH) ₂	[Zn(NH ₃) ₄] ²⁺
Cd ²⁺	Cd(OH) ₂	[Cd(NH ₃) ₄] ²⁺
Hg ²⁺	Hg(OH) ₂	[Hg(NH ₃) ₄] ²⁺

^aThe ions of Rh, Ir, Pd, Pt, and Au show similar behavior.^bCuOH and AgOH are unstable and decompose to the corresponding oxides.

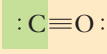
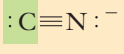
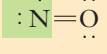
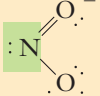
25-3 Important Terms

► The replacement of hydrogen atoms on PH₃ with hydrocarbon groups such as methyl (CH₃) generates phosphines (e.g., P(CH₃)₃), which are very strong ligands for middle to late transition metal atoms. In general, the stronger the donor ability of the lone pair on the ligand, the stronger the dative bond that is formed to the metal atom.

The Lewis bases in coordination compounds may be molecules, anions, or (rarely) cations. They are called *ligands* (Latin *ligare*, “to bind”). The **donor atoms** of the ligands are the atoms that donate shares in electron pairs to metals. In some cases, it is not possible to identify donor atoms because the bonding electrons are not localized on specific atoms. Organic molecules such as ethylene, H₂C=CH₂, bond to a transition metal through the π electrons in their double bonds. In fact, any molecule or ion with π electrons (double or triple bonds) or lone pairs of electrons can act as a ligand to a metal atom or ion. The higher the energy of these electron pairs, the better the donor ability of the ligand and the stronger the metal–ligand bond. Examples of a few simple ligands are listed in Table 25-4.

Ligands that can bond to a metal through only one donor atom at a time are **monodentate** (Latin *dent*, “tooth”). Ligands that have more than one donor linked by other atoms (often carbons) so that the donors can coordinate to the same metal are called

Table 25-4 Typical Simple Ligands with Their Donor Atoms Shaded

Molecule	Name	Name as Ligand	Ion	Name	Name as Ligand
	ammonia	ammine		chloride	chloro
	water	aqua		fluoride	fluoro
	carbon monoxide	carbonyl		cyanide	cyano ^a
	phosphine	phosphine		hydroxide	hydroxo
	nitrogen oxide	nitrosyl		nitrite	nitro ^b

^aNitrogen can also function as a donor atom in a bridging ligand to a second metal center, but only after the carbon atom has bonded to the initial metal center.^bOxygen atoms can also function as donor atoms, in which case the ligand name is “nitrito.”

Unless otherwise noted, all content on this page is © Cengage Learning.

chelates or **chelating ligands**. Chelating ligands that can bond simultaneously through more than one donor atom are **polydentate**. Polydentate ligands that bond through two, three, four, five, or six donor atoms are called *bidentate*, *tridentate*, *quadridentate*, *pentadentate*, and *hexadentate*, respectively. Complexes that consist of a metal atom or ion and polydentate ligands are called *chelate complexes* (Greek *chele*, “claw”). Chelating ligands are considerably less likely to dissociate from the metal compared to monodentate ligands with similar bond strengths due to kinetic effects. If one donor group dissociates, the atoms connecting it to the rest of the ligand keep it in proximity to the metal. This makes it more likely to recoordinate to the metal.

The **coordination number** of a metal atom or ion in a complex is the number of donor atoms to which it is bonded, which is not necessarily the number of ligands. The **coordination sphere** includes the metal or metal ion (called the **central atom**) and its ligands, but no uncoordinated counterions. For example, the coordination sphere of hexaamminecobalt(III) chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, is the hexaamminecobalt(III) ion, $[\text{Co}(\text{NH}_3)_6]^{3+}$. The chloride counterions are not bonded to the Co center and, in this case, are not acting as ligands. These terms are illustrated in Table 25-5.

25-4 Nomenclature

The International Union of Pure and Applied Chemistry (IUPAC) has adopted a set of rules for naming coordination compounds. The rules are based on those originally devised by Werner.

1. Cations are always named before anions, with a space between their names.
2. In naming the coordination sphere, ligands are named in alphabetical order. The prefixes di = 2, tri = 3, tetra = 4, penta = 5, hexa = 6, and so on specify the number of each kind of *simple* (monodentate) ligand. For example, in dichloro, the “di” indicates that two Cl^- ions act as ligands. For complicated ligands (for example, polydentate chelating agents), other prefixes are used, including: bis = 2, tris = 3, tetrakis = 4, pentakis = 5, and hexakis = 6. The names of complicated ligands are enclosed in parentheses. The numeric prefixes are not used in alphabetizing. When a prefix denotes the number of substituents on a single ligand, as in dimethylamine, $\text{NH}(\text{CH}_3)_2$, it is used to alphabetize ligands.
3. The names of anionic ligands end in the suffix -o. Examples are F^- , fluoro; OH^- , hydroxo; O^{2-} , oxo; S^{2-} , sulfido; CO_3^{2-} , carbonato; CN^- , cyano; SO_4^{2-} , sulfato; NO_3^- , nitrate; $\text{S}_2\text{O}_3^{2-}$, thiosulfato.
4. The names of neutral ligands are usually unchanged. Four important exceptions are NH_3 , ammine; H_2O , aqua; CO, carbonyl; and NO, nitrosyl.
5. Some metals exhibit variable oxidation states. The oxidation number of such a metal is designated by a Roman numeral in parentheses following the name of the complex ion or molecule.
6. The suffix “-ate” at the end of the name of the complex signifies that it is an anion. If the complex is neutral or cationic, no suffix is used. The English stem is routinely used for the metal, but where the naming of an anion is awkward, the Latin stem is substituted. For example, “ferrate” is used rather than “ironate,” and “plumbate” rather than “leadate” (Table 25-6).

The following examples illustrate these rules.

$\text{K}_2[\text{Cu}(\text{CN})_4]$	potassium tetracyanocuprate(II)
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	diamminesilver chloride
$[\text{Cr}(\text{OH}_2)_6](\text{NO}_3)_3$	hexaaquachromium(III) nitrate
$[\text{Co}(\text{en})_2\text{Br}_2]\text{Cl}$	dibromobis(ethylenediamine)cobalt(III) chloride
$\text{Na}[\text{Al}(\text{OH})_4]$	sodium tetrahydroaluminate
$\text{Ni}(\text{CO})_4$	tetracarbonylnickel(0)

Table 25-6 Names for Some Metals in Complex Anions

Metal	Name* of Metal in Complex Anions
aluminum	aluminate
antimony	antimonate
chromium	chromate
cobalt	cobaltate
copper	<i>cuprate</i>
gold	<i>aurate</i>
iron	<i>ferrate</i>
lead	<i>plumbate</i>
manganese	manganate
nickel	nickelate
platinum	platinate
silver	<i>argentate</i>
tin	<i>stannate</i>
zinc	zincate

*Stems derived from Latin names for metals are shown in italics.

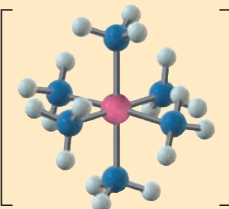
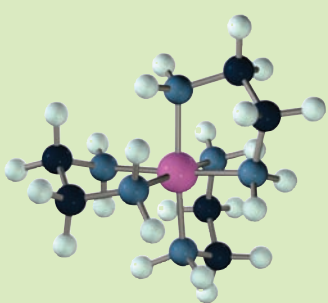
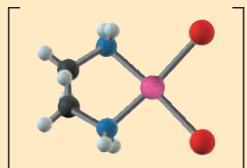
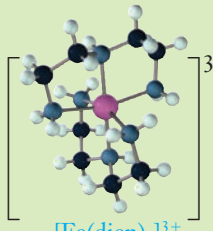
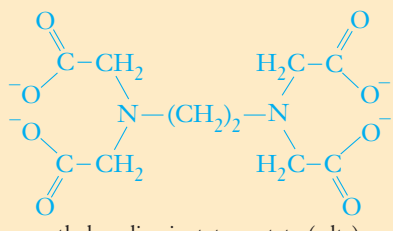
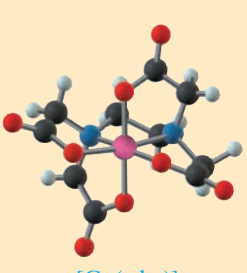
STOP & THINK

The term *ammine* (two m's) signifies the presence of ammonia as a ligand. It is different from the term *amine* (one m), which describes some organic compounds (see Section 23-12) that are derived from ammonia.

► The oxidation state of aluminum is not given because it is always +3.

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 25-5 Some Ligands and Coordination Spheres (complexes)

Ligand(s)	Classification	Coordination Sphere	Coordination Number of M	Oxidation Number of M
NH_3 ammine	monodentate	 $[\text{Co}(\text{NH}_3)_6]^{3+}$ hexamminecobalt(III)	6	+3
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ (or ) ethylenediamine (en)	bidentate	 $[\text{Co}(\text{en})_3]^{3+}$ tris(ethylenediamine)cobalt(III) ion	6	+3
Br^- bromo $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ethylenediamine (en)	monodentate bidentate	 $[\text{Cu}(\text{en})\text{Br}_2]$ dibromoethylenediaminecopper(II)	4	+2
$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{N}(\text{H})-(\text{CH}_2)_2-\text{NH}_2$ (or ) diethylenetriamine (dien)	tridentate	 $[\text{Fe}(\text{dien})_2]^{3+}$ bis(diethylenetriamine)iron(III)ion	6	+3
 ethylenediaminetetraacetato (edta)	hexadentate	 $[\text{Co}(\text{edta})]^-$ (ethylenediaminetetraacetato)-cobaltate(III) ion	6	+3

$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_6]$	tetraammineplatinum(II) hexachloroplatinate(IV)
$\text{K}_4[\text{Ni}(\text{CN})_2(\text{ox})_2]$	potassium dicyanobis(oxalato)nickelate(II)
$[\text{Cu}(\text{NH}_3)_2(\text{en})]\text{Br}_2$	diammine(ethylenediamine)copper(II) bromide
$\text{Na}_2[\text{Sn}(\text{OH})_6]$	sodium hexahydroxostannate(IV)
$[\text{Co}(\text{en})_3](\text{NO}_3)_3$	tris(ethylenediamine)cobalt(III) nitrate
$[\text{Co}(\text{NH}_3)_4(\text{OH}_2)\text{Cl}]\text{Cl}_2$	tetraammineaquachlorocobalt(III) chloride

► The abbreviation ox represents the oxalate ion $(\text{COO})_2^{2-}$ or $\text{C}_2\text{O}_4^{2-}$, which usually functions as a chelating ligand.

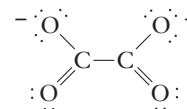


Table 25-7 Idealized Geometries for Various Coordination Numbers

Coordination Number	Geometry	Examples	Model
2	 Linear	$[\text{Ag}(\text{NH}_3)_2]^+$ $[\text{Cu}(\text{CN})_2]^-$ $[\text{Ag}(\text{NH}_3)_2]^+$	
4	 Tetrahedral	$[\text{Zn}(\text{CN})_4]^{2-}$ $[\text{Cd}(\text{NH}_3)_4]^{2+}$ $[\text{Cd}(\text{NH}_3)_4]^{2+}$	
4	 Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ $[\text{Cu}(\text{OH}_2)_4]^{2+}$ $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	
5	 Trigonal bipyramidal	$\text{Fe}(\text{CO})_5$ $[\text{CuCl}_5]^{3-}$ $\text{Fe}(\text{CO})_5$	
5	 Square pyramidal	$[\text{Ni}(\text{CN})_5]^{3-}$ $[\text{MnCl}_5]^{3-}$ $[\text{MnCl}_5]^{3-}$	
6	 Octahedral	$[\text{Fe}(\text{CN})_6]^{4-}$ $[\text{Fe}(\text{OH}_2)_6]^{2+}$ $[\text{Fe}(\text{CN})_6]^{4-}$	

Unless otherwise noted, all content on this page is © Cengage Learning.

25-5 Structures

The structures of coordination compounds are governed largely by the coordination number of the metal. Many have structures similar to the simple molecules and ions we studied in Chapter 8. Unshared pairs of electrons in d orbitals usually have only small influences on geometry because the sizes of the ligand atoms usually dominate. Table 25-7 summarizes the geometries for common coordination numbers.

Both tetrahedral and *square planar* geometries are common for complexes with coordination number 4. Square planar geometries are favored by Rh, Ir, Ni, Pd, Pt, Cu, and Au complexes when the metal is in the d^8 electronic state. Large ligands can lead to distortions away from square planar to tetrahedral. Most other metal complexes with four ligands favor tetrahedral geometries. For coordination number 5, the trigonal bipyramidal structure and the square pyramidal structure are both common. Transition metal complexes with coordination numbers as high as 7, 8, and 9 are known. The geometries shown in Table 25-7 are ideal geometries. Actual structures are sometimes distorted, especially if the ligands are not all the same. The distortions are usually due to larger ligands bumping into one another (*steric effects*) and occasionally due to smaller anionic ligands repelling one another.

Isomerism in Coordination Compounds

As we have seen in Chapters 23 and 24, **isomers** are different compounds that have the same molecular formula; they have the same number and kinds of atoms arranged differently. The term *isomers* comes from the Greek word meaning “same parts.” *Because their structures are different, isomers have different physical and chemical properties.* Here we will extend our discussion of isomerism to include that caused by different arrangements of ligands about central metal ions.

There are two major classes of isomers: structural (constitutional) isomers and stereoisomers. For coordination compounds, each can be further subdivided as follows.

Structural Isomers

1. ionization isomers
2. hydrate isomers
3. coordination isomers
4. linkage isomers

Stereoisomers

1. geometric (positional) isomers
2. optical isomers

1 $[\text{Cr}(\text{CO})_6]$ (white); CO is the ligand.

2 $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_2]$ (green); $(\text{C}_2\text{O}_4)_2^{2-}$ (oxalate ion) is the ligand.

3 $[\text{Co}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]\text{I}_3$ (yellow-orange); ethylenediamine is the ligand.

4 $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]\text{Cl}_3$ (red); NH_3 and H_2O are the ligands.

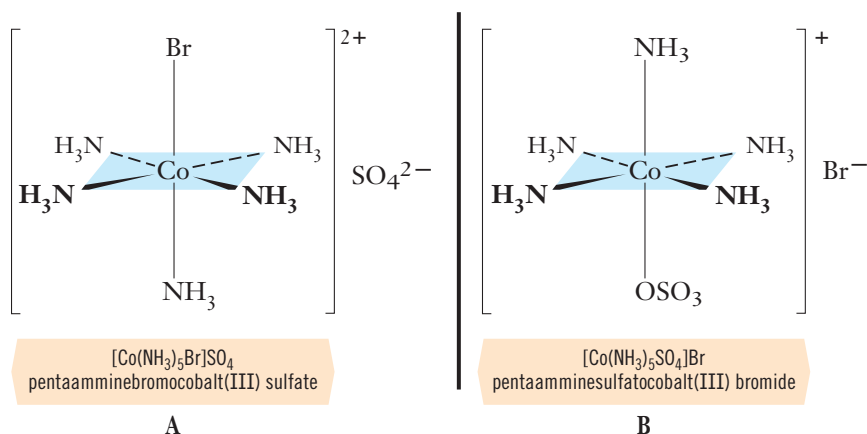
5 $\text{K}_3[\text{Fe}(\text{CN})_6]$ (red-orange); CN^- is the ligand. (A drop of water fell on this sample causing the darker spot.)

Charles D. Winters

Some coordination compounds.

Differences between **structural isomers** involve either more than one coordination sphere or different donor atoms on the same ligand. They contain *different atom-to-atom bonding sequences*. Simple stereoisomers of coordination compounds involve only one coordination sphere.

dination sphere and the same ligands and donor atoms. Before considering stereoisomers, we will describe the four types of structural isomers in the next section.



► Isomers such as those shown here *may or may not* exist in the same solution in equilibrium. Such isomers are often formed by different reactions.

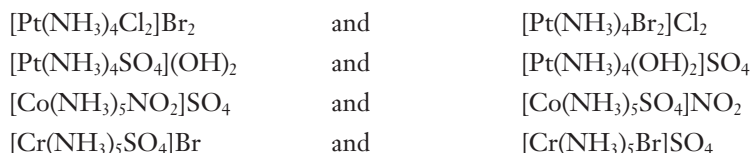
► We write the sulfato ligand as OSO_3 to emphasize that it is coordinated through a lone pair on one of the O atoms.

25-6 Structural (Constitutional) Isomers

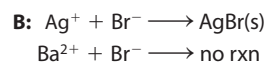
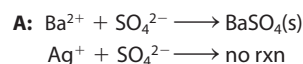
Ionization (Ion–Ion Exchange) Isomers

These isomers result from the interchange of ions inside and outside the coordination sphere. For example, red-violet $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and red $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ shown in the figure above are ionization isomers.

In structure **A**, the SO_4^{2-} ion is free and is not bound to the cobalt(III) ion. A solution of **A** reacts readily with a solution of barium, BaCl_2 , to precipitate BaSO_4 but does not react readily with AgNO_3 . In structure **B**, the SO_4^{2-} ion is bound to the cobalt(III) ion and so it does not react with BaCl_2 in aqueous solution. The Br^- ion is free, however, and a solution of **B** reacts with AgNO_3 to precipitate AgBr . *Equimolar* solutions of **A** and **B** also have different electrical conductivities. The sulfate solution, **A**, conducts electric current better because its ions have 2+ and 2− charges rather than 1+ and 1−. Other examples of this type of isomerism include

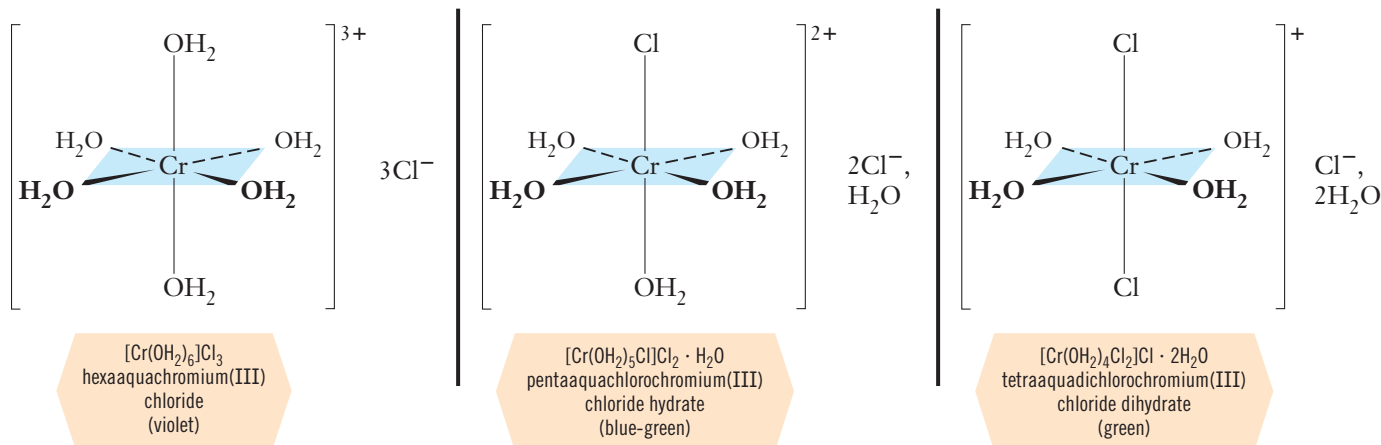


► Recall that BaSO_4 ($K_{\text{sp}} = 1.1 \times 10^{-10}$) and AgBr ($K_{\text{sp}} = 3.3 \times 10^{-13}$) are classified as insoluble in H_2O , whereas BaBr_2 is soluble and Ag_2SO_4 ($K_{\text{sp}} = 1.7 \times 10^{-5}$) is moderately soluble.



Hydrate Isomers

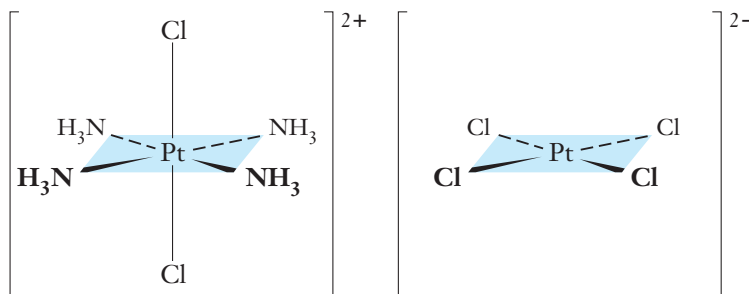
In some crystalline complexes, water can be *inside* or *outside* the coordination sphere. For example, when treated with excess $\text{AgNO}_3(\text{aq})$, solutions of the following three hydrate isomers yield three, two, and one mole of AgCl precipitate, respectively, per mole of complex. The Ag cations react quickly only with the “free” chloride anions that are not coordinated to the Cr atom.



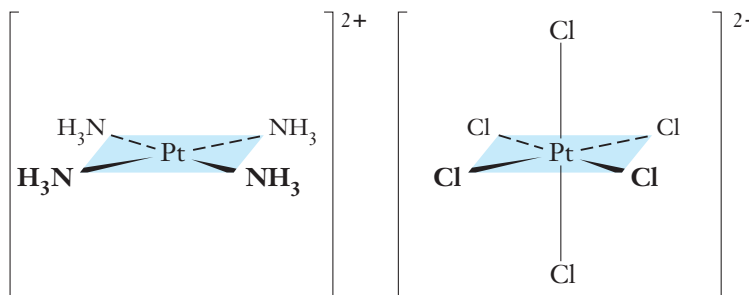
Unless otherwise noted, all content on this page is © Cengage Learning.

Coordination Isomers

Coordination isomerism can occur in compounds containing both complex cations and complex anions. Such isomers involve exchange of ligands between cation and anion, that is, between coordination spheres. An example of coordination isomers appears below.



$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]_2$,
tetraamminedichloroplatinum(IV) tetrachloroplatinate(II)



$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_6]_2$,
tetraammineplatinum(II) hexachloroplatinate(IV)

Two coordination isomers.

Linkage Isomers

Certain ligands can bind to metal ions in more than one way. One example of such a ligand is nitro, —NO_2^- , and nitrito, —ONO^- . The donor atom is written first in the chemical formula. An example of linkage isomers is shown on page 1001.

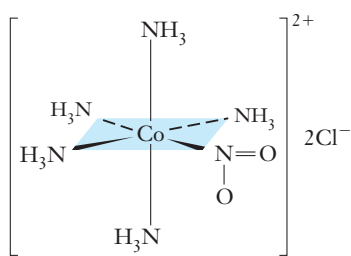
25-7 Stereoisomers

► A complex with coordination number 2 or 3 that contains only *simple ligands* can have only one spatial arrangement. Try building models to see this.

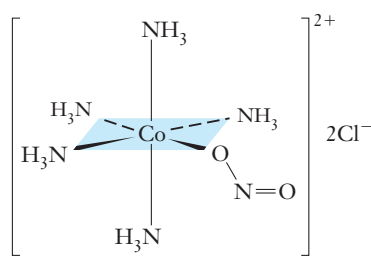
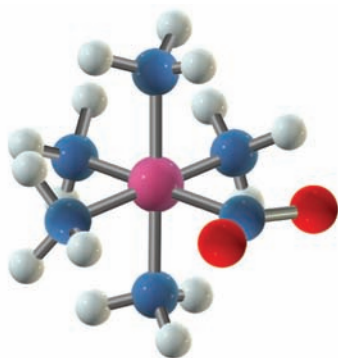
Compounds that contain the same atoms and the same atom-to-atom bonding sequences, but differ only in the spatial arrangements of the atoms relative to the central atom, are **stereoisomers**. Complexes with only *simple* ligands can exist as stereoisomers *only if* they have coordination number 4 or greater. The most common coordination numbers among metal complexes are 4 and 6, so they will be used to illustrate stereoisomerism.

Geometric (*cis-trans*) Isomers

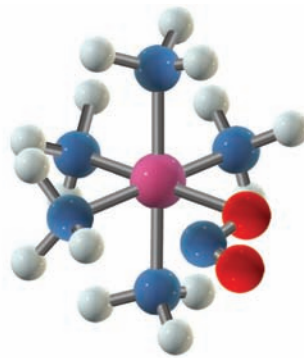
In **geometric isomers**, or ***cis-trans* isomers**, of *coordination compounds*, the same ligands are arranged in different orders within the coordination sphere. Geometric isomerism occurs when atoms or groups of atoms can be arranged on two sides of a rigid structure. *Cis* means “adjacent to” and *trans* means “on the opposite side of.” *Cis*- and *trans*-diamminedichloroplatinum(II) are shown here.



[Co(NH₃)₅NO₂]Cl₂
pentaamminenitrocobalt(III)
chloride
(yellow, stable in acids)

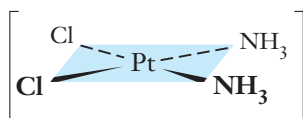


[Co(NH₃)₅ONO]Cl₂
pentaamminenitritocobalt(III)
chloride
(red, decomposes in acids)

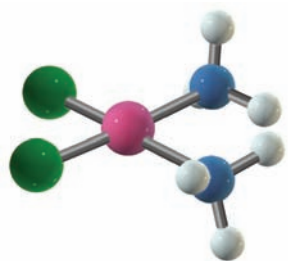


Two linkage isomers.

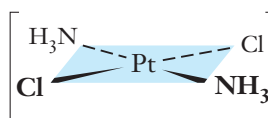
In the *cis* isomer, the chloro groups are closer to each other (on the same side of the square) than they are in the *trans* isomer. The ammine groups are also closer together in the *cis* complex.



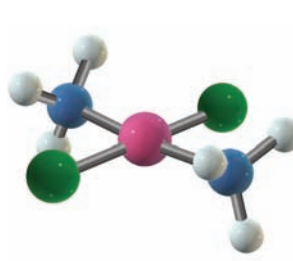
cis
pale yellow
Cl — Pt — Cl angle $\approx 90^\circ$
N — Pt — N angle $\approx 90^\circ$



cis-diamminedichloroplatinum(II),
cis-[Pt(NH₃)₂Cl₂]



trans
dark yellow
Cl — Pt — Cl angle $\approx 180^\circ$
N — Pt — N angle $\approx 180^\circ$

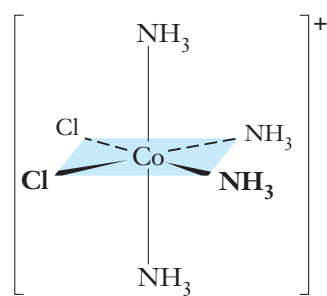


trans-diamminedichloroplatinum(II),
trans-[Pt(NH₃)₂Cl₂]

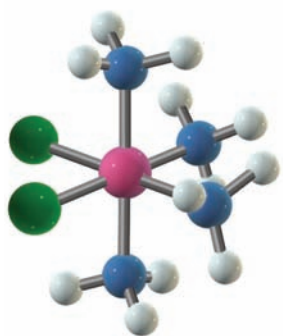
► *Cis-trans* isomerism is not possible for tetrahedral complexes, in which all angles are (ideally) 109.5° .

► The *cis* isomer (known in medicine as "cisplatin") has been used successfully in cancer chemotherapy. The *trans* isomer has no such activity.

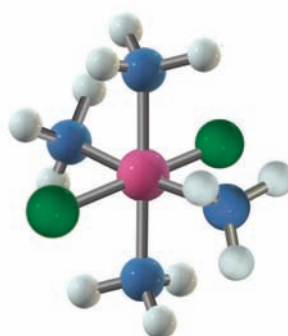
Geometric isomerism is possible for octahedral complexes. For example, complexes of the type MA₄B₂ can exist in two isomeric forms. Consider as an example the complex ion [Co(NH₃)₄Cl₂]⁺. The two like ligands (Cl[−]) can be either *cis* or *trans* to each other. These two complexes are different colors: solutions and salts of the *cis* isomer are violet and those of the *trans* isomer are green.



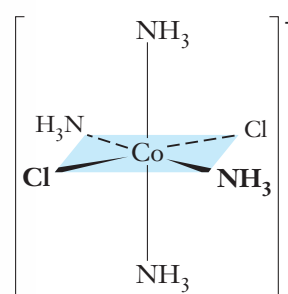
cis-tetraamminedichlorocobalt(III) ion,
 $cis-[Co(NH_3)_4Cl_2]^+$



Ball-and-stick model of *cis*- $[Co(NH_3)_4Cl_2]^+$. Note the positions of the green chloride ligands.



Ball-and-stick model of *trans*- $[Co(NH_3)_4Cl_2]^+$. Note the positions of the green chloride ligands.



trans-tetraamminedichlorocobalt(III) ion,
 $trans-[Co(NH_3)_4Cl_2]^+$

Complexes involving bidentate ligands such as ethylenediamine can also exhibit this kind of isomerism, as shown in Figure 25-2.

Octahedral complexes with the general formula MA_3B_3 can exhibit another type of geometric isomerism, called *mer-fac* isomerism. This can be illustrated with the complex ion $[Pt(NH_3)_3Cl_3]^+$ (see Table 25-2). In one isomer the three similar ligands (e.g., the Cl^- ligands) lie at the corners of a triangular face of the octahedron; this is called the *fac* isomer (for *facial*). In the other isomer, the three similar ligands lie in the same plane; this is called the *mer* isomer (so called because the plane is analogous to a meridian on a globe) (Figure 25-3).

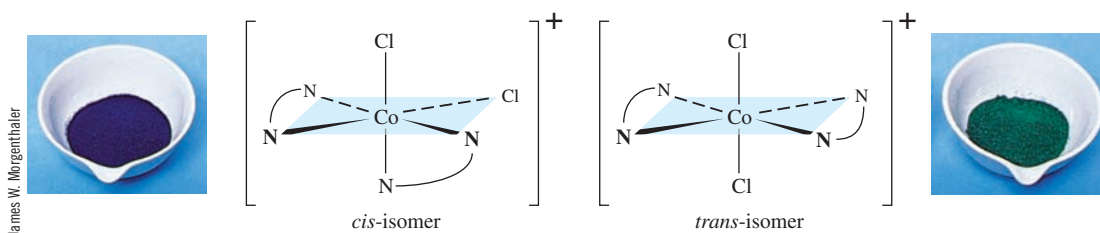
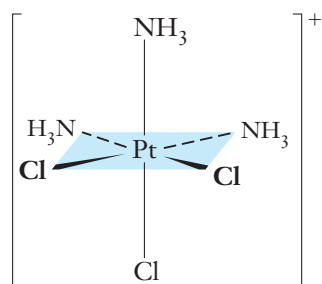
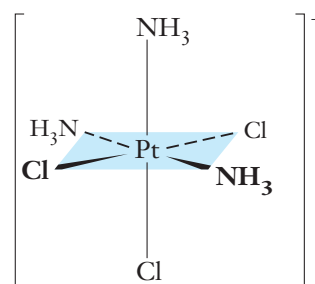
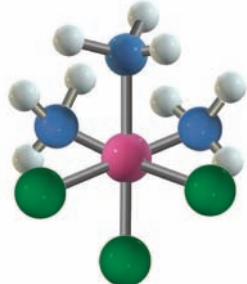


Figure 25-2 The dichlorobis(ethylenediamine)cobalt(III) ion, $[Co(en)_2Cl_2]^+$, exists as a pair of

cis-trans isomers. Ethylenediamine is represented as $\text{N} \text{---} \text{N}$. *Cis*-dichlorobis(ethylenediamine)cobalt(III) perchlorate, $[Co(en)_2Cl_2]ClO_4$, is purple. *Trans*-dichlorobis(ethylenediamine)cobalt(III) chloride, $[Co(en)_2Cl_2]Cl$, is green.



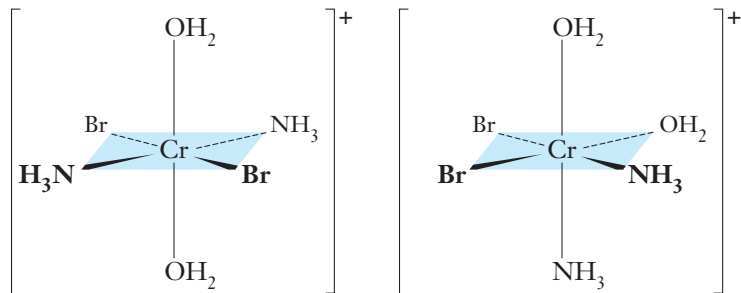
fac-triamminetrichloroplatinum(IV) ion,
 $fac-[Pt(NH_3)_3Cl_3]^+$



mer-triamminetrichloroplatinum(IV) ion,
 $mer-[Pt(NH_3)_3Cl_3]^+$

Figure 25-3 Ball-and-stick models of *fac*- $[Pt(NH_3)_3Cl_3]^+$ (left) and *mer*- $[Pt(NH_3)_3Cl_3]^+$ (right). The three chloro ligands in the *fac*-isomer are all on one triangular face of an octahedron, and the three ammine ligands are all on the opposite triangular face. The *mer* isomer has the chloro ligands in one meridian (in a plane) and the three ammine ligands in a perpendicular meridian.

Complexes of the type $[MA_2B_2C_2]^+$ can exist in several isomeric forms. Consider as an example $[\text{Cr}(\text{OH}_2)_2(\text{NH}_3)_2\text{Br}_2]^+$ shown below. First, the members of all three pairs of like ligands may be either *trans* to each other (**A**) or *cis* to each other (**B**).



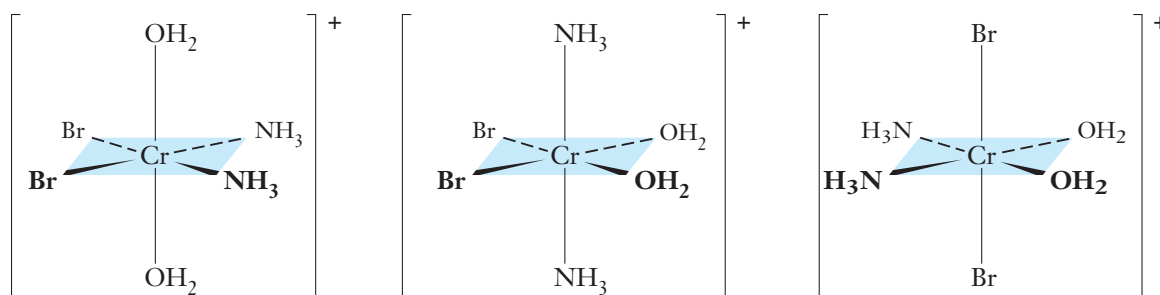
trans-diammine-*trans*-diaqua-*trans*-dibromochromium(III) ion

A

cis-diammine-*cis*-diaqua-*cis*-dibromochromium(III) ion

B

Then, members of one of the pairs may be *trans* to each other, but the members of the other two pairs are *cis*.



cis-diammine-*trans*-diaqua-*cis*-dibromochromium(III) ion

C

trans-diammine-*cis*-diaqua-*cis*-dibromochromium(III) ion

D

cis-diammine-*cis*-diaqua-*trans*-dibromochromium(III) ion

E

In **C**, only the two H_2O ligands are in a *trans* arrangement; in **D**, only the NH_3 ligands are *trans*; and in **E**, only the two Br^- ligands are *trans*.

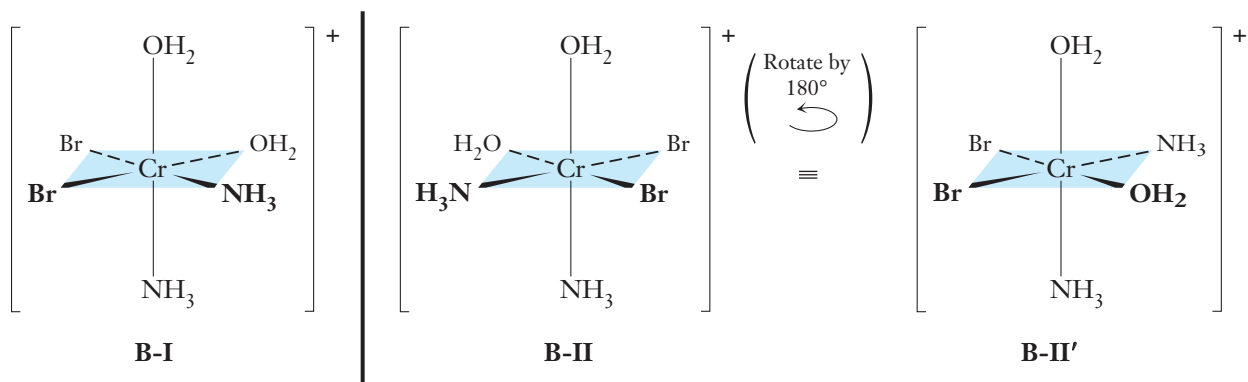
Further interchange of the positions of the ligands produces no new geometric isomers. However, one of the five geometric isomers (**B**) can exist in two distinct forms called *optical isomers*.

► There is no *trans-trans-cis* isomer. Why?

Optical Isomers

The *cis*-diammine-*cis*-diaqua-*cis*-dibromochromium(III) geometrical isomer (**B**) exists in two forms that bear the same relationship to each other as left and right hands. They are *non-superimposable* mirror images of each other and are called **optical isomers** or **enantiomers**.

► An object that is not superimposable with its mirror image is said to be *chiral* (see Section 24-2).



Optical isomers of *cis*-diammine-*cis*-diaqua-*cis*-dibromochromium(III) ion

Unless otherwise noted, all content on this page is © Cengage Learning.

► Alfred Werner was also the first person to demonstrate optical activity in an inorganic compound (not of biological origin). This demonstration silenced critics of his theory of coordination compounds, and he considered this his greatest achievement. Louis Pasteur had demonstrated the phenomenon of optical activity many years earlier in organic compounds of biological origin.

Complexes **B-I** and **B-II** are mirror images of each other. To see that they are not identical, imagine rotating **B-II** about its vertical axis by 180° (**B-II'**) so that the Br^- ligands are both at the left, as they are in **B-I**. Then **B-II'** would have the OH_2 ligand at the right front position and the NH_3 ligand at the right rear position, which is not the same as in **B-I**. No rotation of **B-II** makes it identical to **B-I**. Thus, these two arrangements are nonsuperimposable mirror images of each other. Ball-and-stick models of these two complexes are shown in Figure 25-4.

Optical isomers interact with polarized light in different ways. Separate equimolar solutions of each enantiomer rotate *plane-polarized light* (Figures 25-5 and 25-6) by equal amounts but in opposite directions. One solution is **dextrorotatory** (rotates light to the *right*) and the other is **levorotatory** (rotates light to the *left*). Optical isomers are called

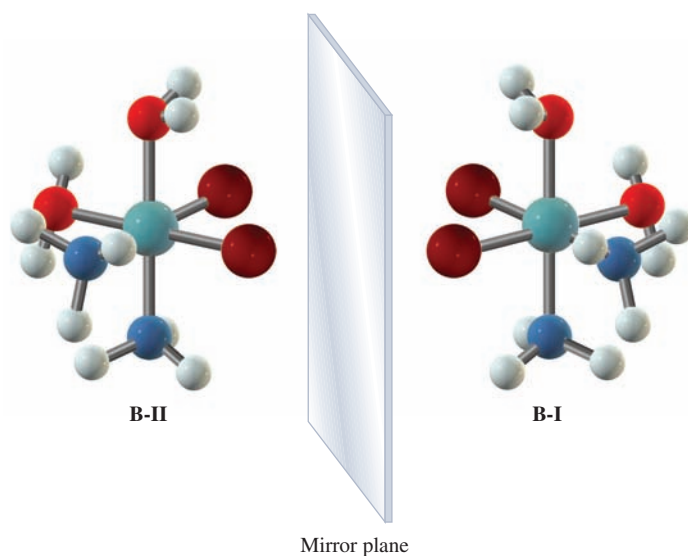


Figure 25-4 Models of the optical isomers of the *cis*-diammine-*cis*-diaqua-*cis*-dibromochromium(III) ion.

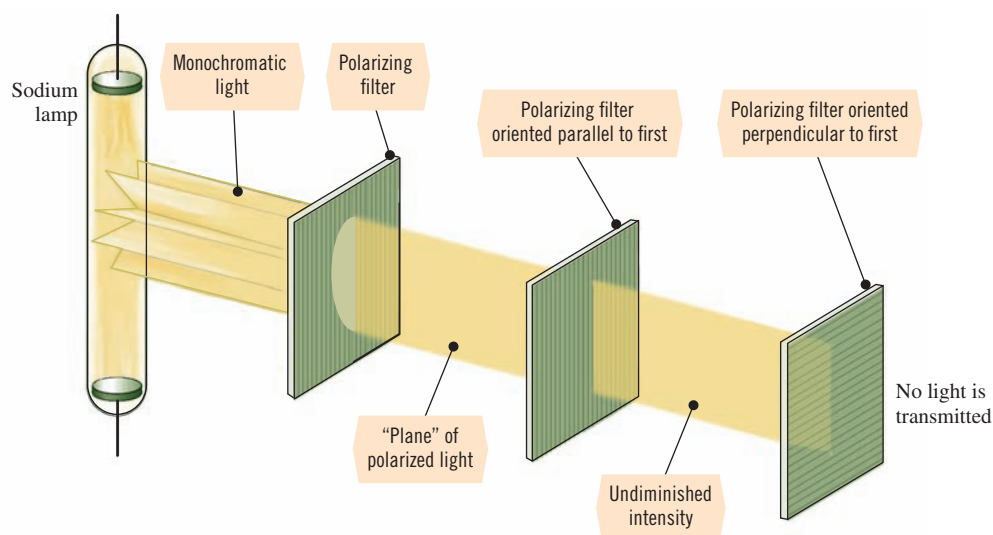


Figure 25-5 Light from a lamp or from the sun consists of electromagnetic waves that vibrate in all directions perpendicular to the direction of travel. Polarizing filters absorb all waves except those that vibrate in a single plane. All of this plane-polarized light passed by the first polarizing filter is also passed by the second, parallel filter. The third polarizing filter, with a plane of polarization at right angles to the first, absorbs the polarized light completely.

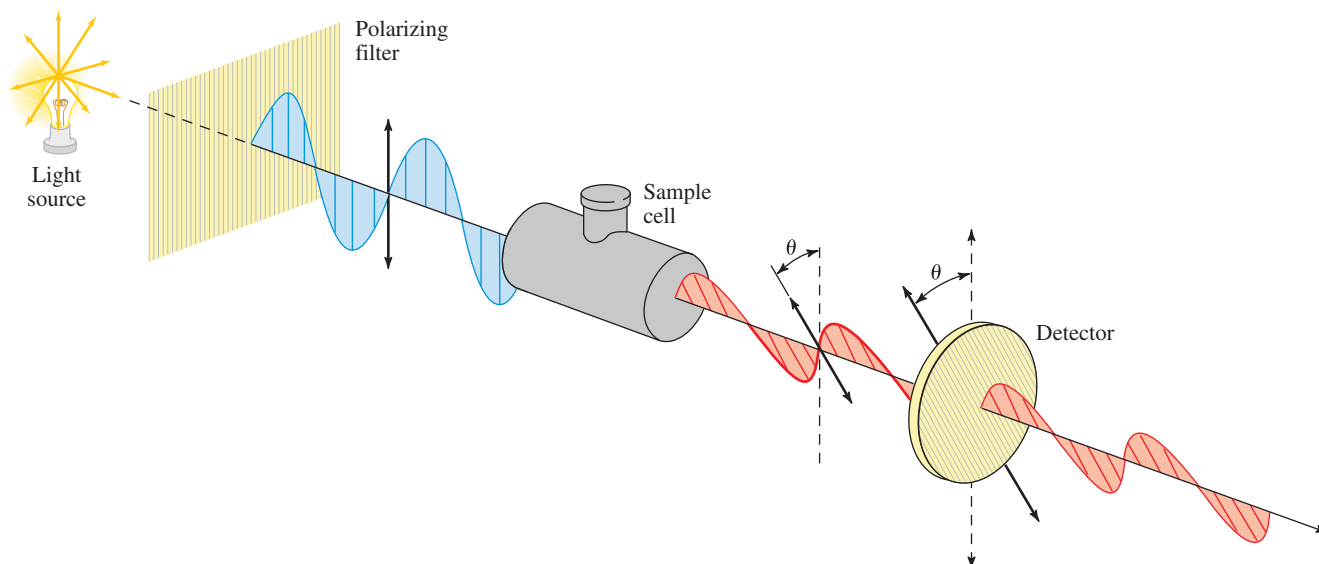
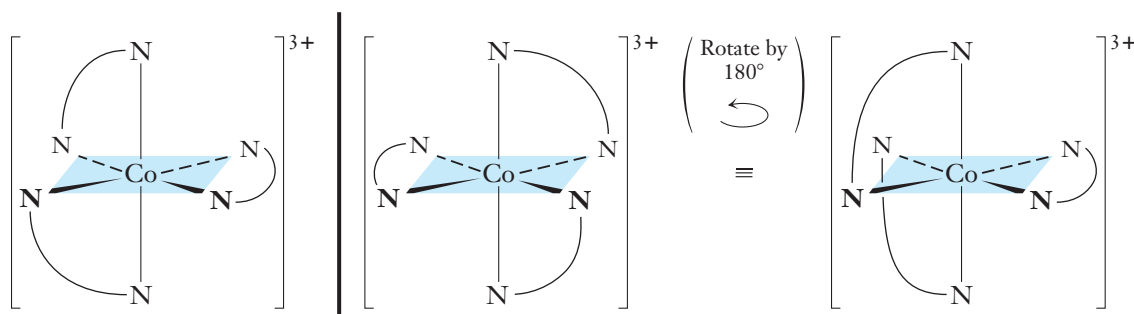


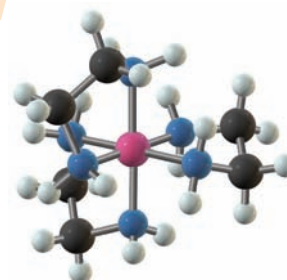
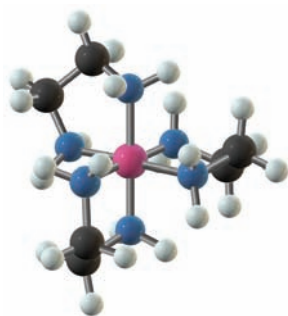
Figure 25-6 The principles of a **polarimeter**. The plane of polarization of plane-polarized light is rotated through an angle (θ) as it passes through an optically active medium. Species that rotate the plane to the right (clockwise as shown here) are dextrorotatory, and those that rotate it to the left are levorotatory.

dextro and *levo* isomers. The phenomenon by which plane-polarized light is rotated is called **optical activity**. It can be measured with a device called a polarimeter (see Figure 25-6) or with more sophisticated instruments. A single solution containing equal amounts of the two isomers is a **racemic mixture**. The equal and opposite effects of the two isomers exactly cancel, so this solution does not rotate plane-polarized light. To exhibit optical activity, the *dextro* and *levo* isomers must be separated from each other. This is done by one of a number of chemical or physical processes broadly called *optical resolution*.

Another pair of optical isomers follows, each of which contains three bidentate ethylenediamine ligands.



The two optical isomers of the *tris*(ethylenediamine)cobalt(III) ion



Unless otherwise noted, all content on this page is © Cengage Learning.

Bonding in Coordination Compounds

Bonding theories for coordination compounds should be able to account for structural features, colors, and magnetic properties. The earliest accepted theory was the valence bond theory (see Chapter 8). It can account for structural and magnetic properties, but it offers no explanation for the wide range of colors of coordination compounds. The **crystal field theory** gives satisfactory explanations of color, as well as of structure and magnetic properties, for many coordination compounds. We will therefore discuss only this theory in the remainder of this chapter.

25-8 Crystal Field Theory

► Modern ligand field theory is based on crystal field theory. It attributes partial covalent character and partial ionic character to bonds. It is a more sophisticated theory, but too complicated to present here.

► The labels e_g (for $d_{x^2-y^2}$, d_{z^2}) and t_{2g} (for d_{xy} , d_{yz} , d_{xz}) refer to the symmetry of those sets of d orbitals in an octahedral complex.

► Recall that degenerate orbitals are orbitals of equal energy.

► The t_{2g} orbitals were originally in a uniform spherical repulsive electric field. This changes because the incoming ligands localize the electric field and orient it directly toward the two e_g orbitals. As a result, the t_{2g} orbitals are now exposed to a less repulsive electric field, so they drop in energy (become more stable).

Hans Bethe (1906–2005) and J. H. van Vleck (1899–1980) developed the crystal field theory between 1919 and the early 1930s. It was not widely used, however, until the 1950s. In its original form, it assumed that the bonds between ligand and metal were completely ionic.

In a metal ion surrounded by ligands, the d orbitals are at higher energy than they are in an isolated metal ion. If the surrounding electrons were uniformly distributed about the metal ion, the energies of *all* five d orbitals would increase by the same amount (a *spherical crystal field*). Because the ligands approach the metal ion from different directions, they affect different d orbitals in different ways. In this chapter, we will illustrate the application of these ideas to complexes with coordination number 6 (*octahedral crystal field*).

The $d_{x^2-y^2}$ and d_{z^2} orbitals are directed along a set of mutually perpendicular x , y , and z axes (see Figure 5-25). As a group, these orbitals are called **e_g orbitals**. The d_{xy} , d_{yz} , and d_{xz} orbitals, collectively called **t_{2g} orbitals**, lie between the axes. The ligand donor atoms approach the metal ion along the axes to form octahedral complexes. Crystal field theory proposes that the approach of the six donor atoms (point charges) along the x , y , and z axes sets up an electric field (the crystal field). Electrons on the ligands repel electrons in e_g orbitals on the metal ion more strongly than they repel those in the t_{2g} orbitals (Figure 25-7). This removes the degeneracy of the set of d orbitals and splits them into two sets, the e_g set at higher energy and the t_{2g} set at lower energy.

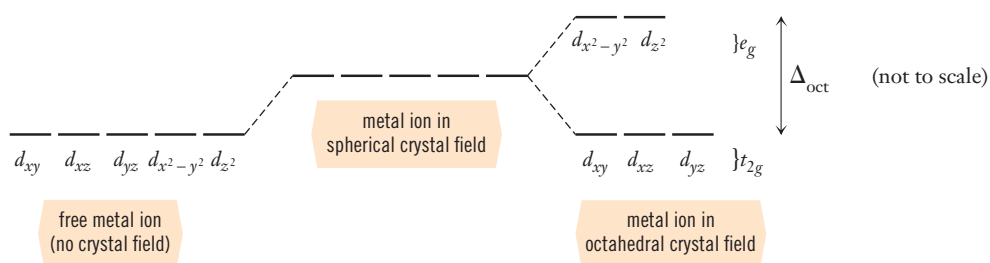
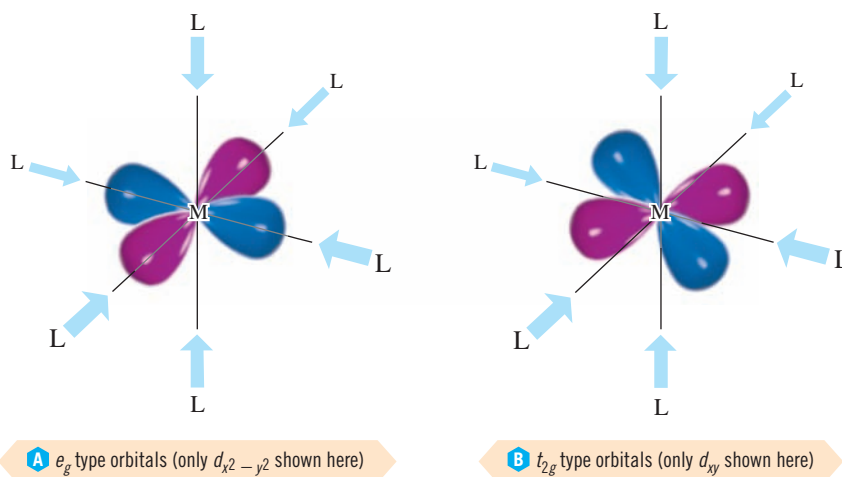


Figure 25-7 Effects of the approach of ligands on the energies of d orbitals on the metal ion. In an octahedral complex, the ligands (L) approach the metal ion (M) along the x , y , and z axes, as indicated by the blue arrows. (a) The orbitals of the e_g type— $d_{x^2-y^2}$ (shown here) and d_{z^2} —point directly toward the incoming ligands, so electrons in these orbitals are strongly repelled. (b) The orbitals of the t_{2g} type— d_{xy} (shown here), d_{xz} , and d_{yz} —do not point toward the incoming ligands, so electrons in these orbitals are less strongly repelled.



Unless otherwise noted, all content on this page is © Cengage Learning.

The energy separation between the two sets of orbitals is called the **crystal field splitting energy**, $\Delta_{\text{octahedral}}$, or Δ_{oct} . It is proportional to the *crystal field strength* of the ligands—that is, how strongly the ligand electrons repel the electrons on the metal ion. In modern bonding terms, the more strongly the ligands coordinate or bond to the metal atom, the larger the energy gap between the e_g and t_{2g} orbitals.

The d electrons on a metal ion occupy the t_{2g} set in preference to the higher energy e_g set. Electrons that occupy the e_g orbitals are strongly repelled by the relatively close approach of ligands. The occupancy of these orbitals tends to destabilize octahedral complexes.

As always, electrons occupy the orbitals in the arrangement that results in the lowest energy. The electron **pairing energy**, P , is the expenditure of energy that is necessary to pair electrons by bringing two negatively charged particles into the same region of space. We must compare this with the crystal field splitting energy, Δ_{oct} , the difference in energy between t_{2g} and e_g orbitals. **Weak field ligands** (such as F^-) cause only small splitting energies, whereas **strong field ligands** (such as CN^-) give large values of Δ_{oct} .

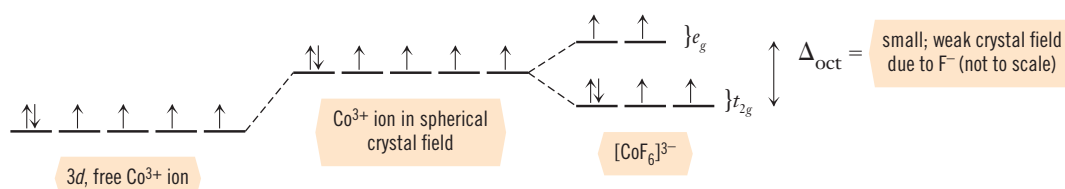
If the splitting energy, Δ_{oct} , is smaller than the pairing energy, P , the electrons occupy all five nondegenerate orbitals singly before pairing. After all d orbitals are half-filled, additional electrons then pair with electrons in the lower energy t_{2g} set. Such a complex would have the same number of *unpaired* electrons on the metal atom or ion as when the metal is uncomplexed; this is called a **high spin complex**. But if the orbital splitting energy is greater than the pairing energy, the electrons will be at lower energy if they pair in the t_{2g} orbital before any electrons occupy the higher energy e_g orbitals. Such a complex could have fewer unpaired electrons on the metal atom than when the metal is uncomplexed, so it is called a **low spin complex**.

Let us now describe the hexafluorocobaltate(III) ion, $[\text{CoF}_6]^{3-}$, and the hexacyanocobaltate(III) ion, $[\text{Co}(\text{CN})_6]^{3-}$. Both contain the $d^6 \text{Co}^{3+}$ ion. The $[\text{CoF}_6]^{3-}$ ion is a paramagnetic complex, whereas $[\text{Co}(\text{CN})_6]^{3-}$ is a diamagnetic complex. We will focus our attention on the d electrons.

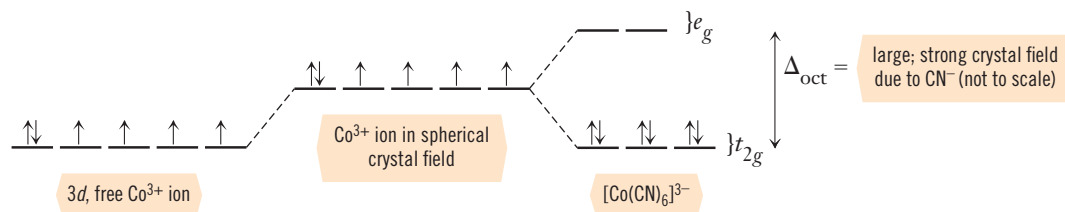
The free Co^{3+} ion has six electrons (four unpaired) in its $3d$ orbitals.



Magnetic measurements indicate that $[\text{CoF}_6]^{3-}$ also has four unpaired electrons per ion. So there must be four electrons in t_{2g} orbitals and two electrons in e_g orbitals. Fluoride, F^- , is a weak field ligand, so the crystal field splitting energy is very small ($\Delta_{\text{oct}} < P$) and electron pairing is unfavorable. Thus $[\text{CoF}_6]^{3-}$ is a *high spin* complex.



On the other hand, $[\text{Co}(\text{CN})_6]^{3-}$ is diamagnetic, so all six d electrons must be paired in the t_{2g} orbitals. Cyanide ion, CN^- , is a strong field ligand, which generates a large crystal field splitting energy ($\Delta_{\text{oct}} > P$), making electron pairing more favorable; therefore, $[\text{Co}(\text{CN})_6]^{3-}$ is a *low spin* complex.



The difference in electron configurations between $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{3-}$ is due to the relative magnitudes of the crystal field splitting, Δ_{oct} , caused by the different crystal field

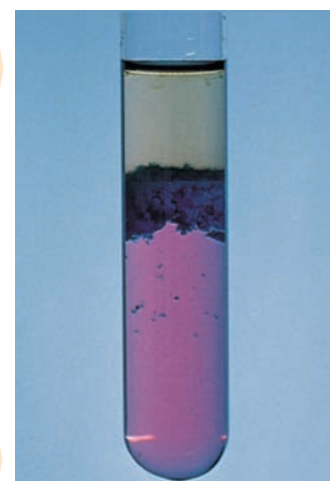
► Typical values of Δ_{oct} are between 100 and 400 kJ/mol. See Key Terms for a more general definition of crystal field splitting energy.

► Weak field ligands bond weakly, while strong field ligands usually coordinate strongly.

► See Key Terms for more general definitions of high spin complex and low spin complex.

► A diamagnetic species has no unpaired electrons. A paramagnetic species has one or more unpaired electrons, and the strength of the paramagnetism depends on the number of unpaired electrons (see Chapter 5).

► $[\text{CoF}_6]^{3-}$ is a *high spin* complex.



$[\text{Co}(\text{OH}_2)_6]^{2+}$ ions are pink (*bottom*). A limited amount of aqueous ammonia produces $\text{Co}(\text{OH})_2$, a blue compound that quickly turns gray (*middle*). $\text{Co}(\text{OH})_2$ dissolves in excess aqueous ammonia to form $[\text{Co}(\text{NH}_3)_6]^{2+}$ ions, which are yellow-orange (*top*).

James W. Mergenthaler

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 25-8 Metal Ion Configurations in High and Low Spin Octahedral Complexes

d^n	Examples	High Spin	Low Spin	d^n	Examples	High Spin	Low Spin
d^1	Ti^{3+}	— — e_g ↑ — — t_{2g}	same as high spin	d^6	Fe^{2+} , Ru^{2+} , Pd^{4+} , Rh^{3+} , Co^{3+}	↑ ↑ e_g ↓ ↓ ↑ t_{2g}	— — e_g ↓ ↓ ↓ t_{2g}
d^2	Ti^{2+} , V^{3+}	— — e_g ↑ ↑ — t_{2g}	same as high spin	d^7	Co^{2+} , Rh^{2+}	↑ ↑ e_g ↓ ↓ ↑ t_{2g}	↑ — e_g ↓ ↓ ↓ t_{2g}
d^3	V^{2+} , Cr^{3+}	— — e_g ↑ ↑ ↑ t_{2g}	same as high spin	d^8	Ni^{2+} , Pt^{2+}	↑ ↑ e_g ↓ ↓ ↓ t_{2g}	same as high spin
d^4	Mn^{3+} , Re^{3+}	↑ — e_g ↑ ↑ ↑ t_{2g}	— — e_g ↓ ↑ ↑ t_{2g}	d^9	Cu^{2+}	↓ ↑ e_g ↓ ↓ ↓ t_{2g}	same as high spin
d^5	Mn^{2+} , Fe^{3+} Ru^{3+}	↑ ↑ e_g ↑ ↑ ↑ t_{2g}	— — e_g ↓ ↓ ↑ t_{2g}	d^{10}	Zn^{2+} , Ag^+ , Hg^{2+}	↓ ↓ e_g ↓ ↓ ↓ t_{2g}	same as high spin

strengths of F^- and CN^- . The CN^- ion interacts with vacant metal orbitals more strongly than the F^- ion does. As a result, the crystal field splitting generated by the close approach of six CN^- ions (strong field ligands) to the metal ion is greater than that generated by the approach of six F^- ions (weak field ligands).

► $[\text{Co}(\text{CN})_6]^{3-}$ is a *low spin* complex.

► A convenient way to describe d -transition metal ions is to indicate the number of d electrons, which is directly related to the oxidation state of the metal atom.

$$\Delta_{\text{oct}} \text{ for } [\text{Co}(\text{CN})_6]^{3-} > \Delta_{\text{oct}} \text{ for } [\text{CoF}_6]^{3-}$$

Different metal ion configurations are possible only for octahedral complexes having metal ions with d^4 , d^5 , d^6 , and d^7 configurations. For d^1 – d^3 and d^8 – d^{10} octahedral ions, only one possibility exists and is designated as high spin. All d^n possibilities are shown in Table 25-8.

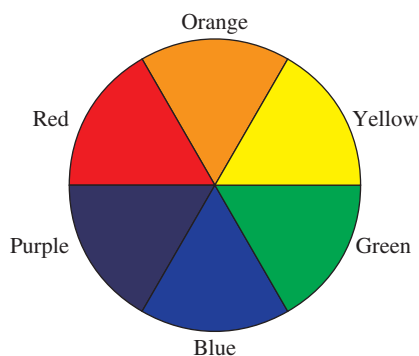
25-9 Color and the Spectrochemical Series

A substance appears colored because it absorbs light that corresponds to one or more of the wavelengths in the visible region of the electromagnetic spectrum (4000 to 7000 Å) and transmits or reflects the other wavelengths. Our eyes are detectors of light in the visible region, and so each wavelength in this region appears as a different color. A combination of all wavelengths in the visible region is called “white light”; sunlight is an example. The absence of all wavelengths in the visible region is blackness.

Table 25-9 shows the relationships among some colors absorbed and colors transmitted or reflected in the visible region. The first column displays the wavelengths absorbed. The **spectral color** is the color associated with the wavelengths of light absorbed by the sample. When certain visible wavelengths are absorbed from incoming “white” light, the light *not absorbed* remains visible to us as transmitted or reflected light. For instance, a sample that absorbs orange light appears blue. The **complementary color** is the color associated

Table 25-9 Complementary Colors

Wavelength Absorbed (Å)	Spectral Color (color absorbed)	Complementary Color (color observed)
4100	violet	lemon yellow
4300	indigo	yellow
4800	blue	orange
5000	blue-green	red
5300	green	purple
5600	lemon yellow	violet
5800	yellow	indigo
6100	orange	blue
6800	red	blue-green



A simplified color wheel shows colors and their complementary colors. For example, orange is the complementary color of blue. The data in Table 25-9 are given for specific wavelengths. Broad bands of wavelengths are shown in this color wheel.

Unless otherwise noted, all content on this page is © Cengage Learning.

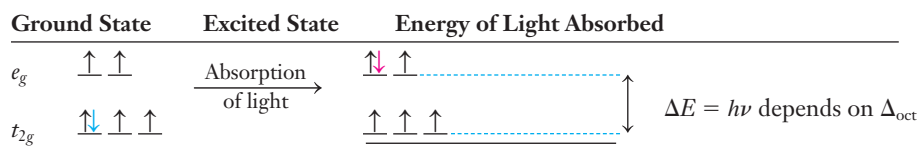
with the wavelengths that are *not* absorbed by the sample. The complementary color is seen when the spectral color is removed from white light.

Most transition metal compounds are colored, a characteristic that distinguishes them from most compounds of the representative elements. In transition metal compounds, the *d* orbitals are often split into two sets of orbitals separated by the splitting energies, Δ_{oct} (for an octahedral complex), that correspond to wavelengths of light in the visible region. The absorption of visible light causes electronic transitions between orbitals in these sets. Table 25-10 gives the colors of some transition metal nitrates in aqueous solution. Solutions of representative (A group) metal nitrates are colorless.



The colors of complex compounds that contain a given metal depend on the ligands. The yellow compound at the left is a salt that contains $[\text{Co}(\text{NH}_3)_6]^{3+}$ ions. In the next three compounds, left to right, one NH_3 ligand in $[\text{Co}(\text{NH}_3)_6]^{3+}$ has been replaced by NCS^- (orange), H_2O (red), and Cl^- (purple). The green compound at the right is a salt that contains $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ ions.

One transition of a high spin octahedral Co(III) complex is depicted as follows.

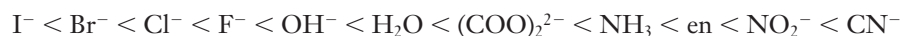


The frequency (ν), and therefore the wavelength and color, of the light absorbed are related to Δ_{oct} . The numerical relationship between Δ_{oct} and the wavelength, λ , of the absorbed light is found by combining the expressions $E = h\nu$ and $\nu = c/\lambda$, where c is the speed of light. For *one* mole of a complex,

$$\Delta_{\text{oct}} = EN_{\text{A}} = \frac{hcN_{\text{A}}}{\lambda} \quad \text{where } N_{\text{A}} \text{ is Avogadro's number}$$

The value of the splitting energy, Δ_{oct} , depends, in turn, on the crystal field strength of the ligands. So the colors and visible absorption spectra of transition metal complexes, as well as their magnetic properties, provide information about the strengths of the ligand–metal interactions.

By interpreting the visible spectra of many complexes, it is possible to arrange common ligands in order of increasing crystal field strengths.



Increasing crystal field strength

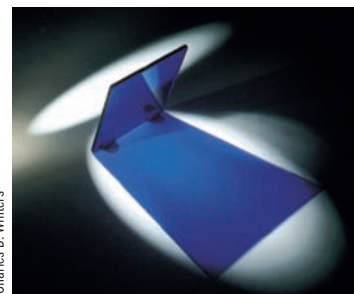
This arrangement is called the **spectrochemical series**. Strong field ligands, such as CN^- , produce large crystal field splittings and usually produce low spin complexes, where possible. Weak field ligands, such as Cl^- , produce small crystal field splittings and high spin complexes. Low spin complexes usually absorb higher-energy (shorter-wavelength) light than do high spin complexes. The colors of several six-coordinate Cr(III) complexes are listed in Table 25-11.

In $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$, the Cr(III) is bonded to six ammonia ligands, which produce a relatively high value of Δ_{oct} . This causes the $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ion to absorb relatively high-energy visible light in the blue and violet regions. Thus, we see yellow-orange, the complementary color.

Table 25-10 Colors of Aqueous Solutions of Some Transition Metal Nitrates

Transition Metal Ion	Observed Color of Aq. Solution
Cr^{3+}	Deep blue
Mn^{2+}	Pale pink
Fe^{2+}	Pale green
Fe^{3+}	Pale purple
Co^{2+}	Pink
Ni^{2+}	Green
Cu^{2+}	Blue

► The electron that is excited by the absorption of light is shown in red.



Adding a Co(II) salt to molten glass gives the glass a deep blue color. This blue glass is often used by glassblowers to block out the intense yellow light emitted by thermally excited sodium atoms present in hot glass.

► We see the light that is transmitted (passed through the sample) or that is reflected by the sample.

Unless otherwise noted, all content on this page is © Cengage Learning.

Water is a weaker field ligand than ammonia, and therefore Δ_{oct} is less for $[\text{Cr}(\text{OH}_2)_6]^{3+}$ than for $[\text{Cr}(\text{NH}_3)_6]^{3+}$. As a result, $[\text{Cr}(\text{OH}_2)_6]\text{Br}_3$ absorbs lower energy (longer wavelength) light. This causes the reflected and transmitted light to be higher-energy bluish gray, the color that describes $[\text{Cr}(\text{OH}_2)_6]\text{Br}_3$.

► Different anions sometimes cause compounds containing the same complex cation to have different colors. For example, two different-colored compounds in this table both contain the $[\text{Cr}(\text{OH}_2)_6]^{3+}$ ion.

Table 25-11 Colors of Some Chromium(III) Complexes

$[\text{Cr}(\text{OH}_2)_6]\text{Cl}_3$	violet	$[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$	yellow
$[\text{Cr}(\text{OH}_2)_6]\text{Br}_3$	bluish gray	$[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	purple
$[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]\text{Cl}$	green	$[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	violet
$[\text{Cr}(\text{OH}_2)_4\text{Br}_2]\text{Br}$	green	$[\text{Cr}(\text{en})_3](\text{SCN})_3$	yellow

KEY TERMS

Ammine complexes Complex species that contain ammonia molecules bonded to metal ions.

Central atom The atom or ion to which the ligands are bonded in a complex species.

Chelate A ligand that utilizes two or more connected donor atoms in bonding to metals.

cis-trans isomerism See *Geometric isomerism*.

Complementary color The color associated with the wavelengths of light that are not absorbed—that is, the color transmitted or reflected.

Complex ion See *Coordination compound or complex*.

Coordinate covalent bond See *Dative bond*.

Coordination compound or complex A compound containing dative bonds between electron pair donors (ligands) and a metal; also known as *Complex ion*.

Coordination isomers Isomers involving exchange of ligands between a complex cation and a complex anion of the same coordination compound.

Coordination number The number of donor atoms coordinated (bonded) to a metal.

Coordination sphere The metal ion and its coordinated ligands, but not any uncoordinated counterions.

Crystal field splitting energy The energy separation between sets of d orbitals in a crystal field. In an octahedral complex, this is denoted by Δ_{oct} and is the energy separation between the e_g and t_{2g} sets of orbitals.

Crystal field theory A theory of bonding in transition metal complexes in which ligands and metal ions are treated as point charges; a purely ionic model. Ligand point charges represent the crystal (electric) field perturbing the metal's d orbitals that contain nonbonding electrons.

Δ_{oct} The energy separation between e_g and t_{2g} sets of metal d orbitals caused by six ligands bonding in an octahedral geometry.

Dative bond A covalent bond in which both shared electrons are donated from the same atom; a bond between a Lewis base and Lewis acid; also known as *Coordinate covalent bond*.

Dextrorotatory Describes an optically active substance that rotates the plane of plane-polarized light to the right (clockwise); also called *dextro*.

Donor atom A ligand atom whose electrons are shared with a Lewis acid.

e_g orbitals A set of $d_{x^2-y^2}$ and d_{z^2} orbitals in an octahedral complex; those d orbitals within a set with lobes directed along the x , y , and z axes.

Enantiomers Stereoisomers that differ only by being nonsuperimposable mirror images of each other, like left and right hands; also known as *Optical isomers*.

Geometric isomerism Occurs when atoms or groups of atoms can be arranged in different ways on two sides of a rigid structure; also known as *cis-trans* isomerism. In geometric isomers of coordination compounds, the same ligands are arranged in different orders within the coordination sphere.

High spin complex A complex in which the crystal field splitting energy is smaller than the pairing energy so that all d orbitals are singly occupied before pairing occurs; there are the same number of unpaired d electrons on the metal atom as when the metal is uncomplexed. In an octahedral high spin complex, all t_{2g} and e_g orbitals are singly occupied before any pairing occurs.

Hydrate isomers Isomers of crystalline complexes that differ in terms of the presence of water inside or outside the coordination sphere.

Ionization isomers Isomers that result from the interchange of ions inside and outside the coordination sphere.

Isomers Different compounds that have the same formula.

Levorotatory Refers to an optically active substance that rotates the plane of plane-polarized light to the left (counterclockwise); also called *levo*.

Ligand A Lewis base in a coordination compound.

Linkage isomers Isomers in which a particular ligand bonds to a metal ion through different donor atoms.

Low spin complex A complex in which the crystal field splitting energy is greater than the pairing energy so that there are the same number or fewer unpaired d electrons on the metal atom than when the metal is uncomplexed. In an octahedral low spin complex, pairing occurs to fill the t_{2g} orbitals before any electrons occupy the e_g orbitals.

Monodentate Describes ligands with only one donor atom.

Optical activity The ability of one of a pair of optical isomers to rotate the plane of polarized light.

Optical isomers See *Enantiomers*.

Pairing energy The energy required to pair two electrons in the same orbital.

Plane-polarized light Light waves in which all the electric vectors are oscillating in one plane.

Polarimeter A device used to measure optical activity.

Polydentate Describes ligands with more than one donor atom.

Racemic mixture An equimolar mixture of optical isomers that is, therefore, optically inactive.

Spectral color The color associated with the wavelengths of light that are absorbed.

Spectrochemical series An arrangement of ligands in order of increasing ligand field strength.

Square planar complex A complex in which the metal atom or ion is in the center of a square plane, with a ligand donor atom at each of the four corners.

Stereoisomers Isomers that differ only in the way in which atoms are oriented in space; they include geometric and optical isomers.

Strong field ligand A ligand that exerts a strong crystal or ligand electric field and generally forms low spin complexes with metal ions when possible. A ligand that forms a strong dative bond.

Structural (constitutional) isomers (Applied to coordination compounds.) Isomers whose differences involve more than a single coordination sphere or else different donor atoms; they include ionization isomers, hydrate isomers, coordination isomers, and linkage isomers.

t_{2g} orbitals A set of d_{xy} , d_{yz} , and d_{xz} orbitals in an octahedral complex; those d orbitals within a set with lobes bisecting (midway between) the x , y , and z axes.

Weak field ligand A ligand that exerts a weak crystal or ligand field and generally forms high spin complexes with metals. A ligand that forms a weak dative bond.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Basic Concepts

1. What property of transition metals allows them to form coordination compounds easily?
2. ● Suggest more appropriate formulas for $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{NH}_3$, and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{NH}_3$.
3. What are the two constituents of a coordination complex? What type of chemical bonding occurs between these constituents?
4. ● Give the coordination number of the central metal ion in (a) $[\text{Pt}(\text{en})_2]^{2+}$ and (b) $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2-}$.
5. ● Distinguish among the terms “ligands,” “donor atoms,” and “chelates.”
6. ● Identify the ligands and give the coordination number and the oxidation number for the central atom or ion in each of the following: (a) $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$; (b) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$; (c) $\text{K}_4[\text{Fe}(\text{CN})_6]$; (d) $[\text{Pd}(\text{NH}_3)_4]^{2+}$.
7. ● Repeat Exercise 6 for (a) $\text{Na}[\text{Au}(\text{CN})_2]$, (b) $[\text{Ag}(\text{NH}_3)_2]^+$, (c) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$, and (d) $[\text{Co}(\text{en})_3]^{3+}$.
8. What is the term given to the phenomenon of ring formation by a ligand in a complex? Describe a specific example.
9. ● Describe the experiments of Alfred Werner on the compounds of the general formula $\text{PtCl}_4 \cdot n\text{NH}_3$, where $n = 2, 3, 4, 5, 6$. What was his interpretation of these experiments?
10. For each of the compounds of Exercise 9, write formulas indicating the species within the coordination sphere. Also indicate the charges on the complex ions.
11. What is the oxidation number of iron, Fe, in each of the following: $\text{Fe}(\text{CO})_5$, $[\text{Fe}(\text{dien})_2]^{3+}$, and $[\text{Fe}(\text{CN})_6]^{4-}$?
12. Atoms of nine elements have been identified in this chapter as capable of being donor atoms in coordination compounds. Name eight of these elements. What do they have in common that allows the atoms to be donor atoms?
13. Name one element that can form different coordination compounds or complex ions in which its atoms have

coordination numbers of two, four, and five. What oxidation number does this element have in each of these species?

14. What one characteristic of the metal in a coordination compound or complex ion primarily determines the geometry of the species? Specifically, why is $[\text{Zn}(\text{CN})_4]^{2-}$ tetrahedral while $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar, and why is $[\text{CuCl}_3]^{3-}$ trigonal bipyramidal while $[\text{MnCl}_3]^{3-}$ is square pyramidal?
15. Write a structural formula showing the ring(s) formed by a bidentate ligand such as ethylenediamine with a metal ion such as Fe^{3+} . How many atoms are in each ring? The formula for this complex ion is $[\text{Fe}(\text{en})_3]^{3+}$.

Ammine Complexes

16. Write net ionic equations for reactions of solutions of the following transition metal salts in water with a *limited amount* of aqueous ammonia: (It is not necessary to show the ions as hydrated.) (a) CuCl_2 ; (b) $\text{Zn}(\text{NO}_3)_2$; (c) $\text{Fe}(\text{NO}_3)_3$; (d) $\text{Co}(\text{NO}_3)_2$; (e) $\text{Ni}(\text{NO}_3)_2$
17. Write *net ionic* equations for the reactions of the insoluble products of Exercise 16 with an *excess* of aqueous ammonia, if a reaction occurs.



Charles D. Winters

$[\text{Cu}(\text{NH}_3)_4]^{2+}$ formation

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

18. Which of the following insoluble metal hydroxides will dissolve in an excess of aqueous ammonia?
 (a) $\text{Zn}(\text{OH})_2$; (b) $\text{Cr}(\text{OH})_3$; (c) $\text{Fe}(\text{OH})_2$; (d) $\text{Ni}(\text{OH})_2$;
 (e) $\text{Cd}(\text{OH})_2$
19. Write net ionic equations for the reactions in Exercise 18.

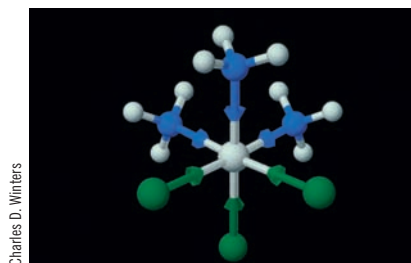
Naming Coordination Compounds

20. Give the oxidation number for the central atom or ion in each of the following complexes.
 (a) $\text{K}_2[\text{Pt}(\text{NO}_2)_4]$
 (b) $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$
 (c) $[\text{Ag}(\text{NH}_3)_2]\text{I}$
 (d) $\text{K}_4[\text{Ni}(\text{CN})_6]$
 (e) $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$
 (f) $\text{Na}[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]$
21. Give the oxidation number for the central atom or ion in each of the following complexes.
 (a) $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5](\text{OH})_2$
 (b) $[\text{Ni}(\text{CO})_4]$
 (c) $\text{Na}_3[\text{CoCl}_6]$
 (d) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 (e) $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{OH})_2\text{Cl}_2]$
 (f) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{I}$
22. Give the name or formula for each ion or compound, as appropriate.
 (a) tetraaquadichlorochromium(III) chloride
 (b) $[\text{Cr}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$
 (c) sodium tetrachlorocobaltate(II)
 (d) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
23. Determine the oxidation state of iron in $\text{KFe}[\text{Fe}(\text{CN})_6]$. Explain your answer.
24. Give systematic names for the following compounds.
 (a) $[\text{Ni}(\text{CO})_4]$
 (b) $\text{Na}_2[\text{Co}(\text{OH})_2(\text{OH})_4]$
 (c) $[\text{Ag}(\text{NH}_3)_2]\text{Br}$
 (d) $[\text{Cr}(\text{en})_3](\text{NO}_3)_3$
 (e) $[\text{Co}(\text{NH}_3)_4\text{Cl}]\text{SO}_4$
 (f) $\text{K}_2[\text{Cu}(\text{CN})_4]$
 (g) $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$
 (h) $\text{Na}[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]$
 (i) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2][\text{Cr}(\text{C}_2\text{O}_4)_2]$
25. Give systematic names for the following compounds.
 (a) $\text{Na}[\text{Au}(\text{CN})_2]$
 (b) $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$
 (c) $[\text{CoCl}_6]^{3-}$
 (d) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 (e) $\text{Na}_2[\text{Pt}(\text{CN})_4]$
 (f) $\text{K}[\text{Cr}(\text{NH}_3)_2(\text{OH})_2\text{Cl}_2]$
 (g) $[\text{Mo}(\text{NCS})_2(\text{en})_2]\text{ClO}_4$
 (h) $[\text{Mn}(\text{NH}_3)_2(\text{OH})_2(\text{OH})]\text{SO}_4$
 (i) $[\text{Co}(\text{en})_2\text{Cl}_2]\text{I}$
26. Give systematic names for the following compounds.
 (a) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$
 (b) $[\text{Fe}(\text{en})_3]\text{PO}_4$
 (c) $[\text{Co}(\text{NH}_3)_6]\text{SO}_4$
 (d) $[\text{Co}(\text{NH}_3)_6]_2(\text{SO}_4)_3$
 (e) $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$
 (f) $(\text{NH}_4)_2[\text{PtCl}_4]$
 (g) $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_2$
 (h) $\text{K}_4[\text{NiF}_6]$
27. Give systematic names for the following compounds.
 (a) $\text{K}_2[\text{PdCl}_6]$
 (b) $(\text{NH}_4)_2[\text{PtCl}_6]$
 (c) $[\text{Co}(\text{en})_3]\text{Cl}_2$
 (d) $\text{Na}_4[\text{Fe}(\text{CN})_6]$
 (e) $[\text{Cr}(\text{en})_2(\text{NH}_3)_2](\text{NO}_3)_2$
 (f) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
 (g) $(\text{NH}_4)_3[\text{CuCl}_5]$
28. Write formulas for the following.
 (a) diamminedichlorozinc
 (b) tin(IV) hexacyanoferrate(II)
 (c) tetracyanoplatinate(II) ion
 (d) potassium hexachlorostannate(IV)
 (e) tetraammineplatinum(II) ion
 (f) sodium hexachloronickelate(II)
 (g) tetraamminecopper(II) pentacyanohydroxoferrate(III)
 (h) diaquadicyanocopper(II)
 (i) potassium hexachloropalladate(IV)
29. Write formulas for the following compounds.
 (a) *trans*-diamminedinitroplatinum(II)
 (b) rubidium tetracyanozincate
 (c) triaqua-*cis*-dibromochlorochromium(III)
 (d) pentacarbonyliron(0)
 (e) sodium pentacyanohydroxocobaltate(III)
 (f) hexammineruthenium(III) tetrachloronickelate(II)
 (g) sodium tetracyanocadmiate
 (h) hexaamminecobalt(III) chloride

Structures of Coordination Compounds

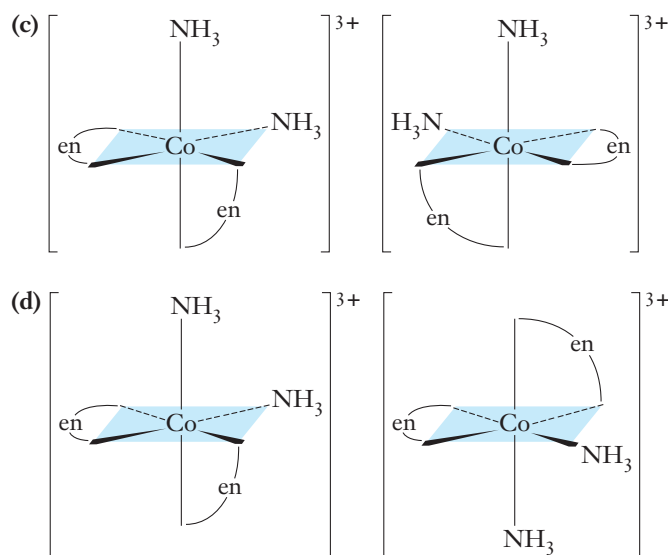
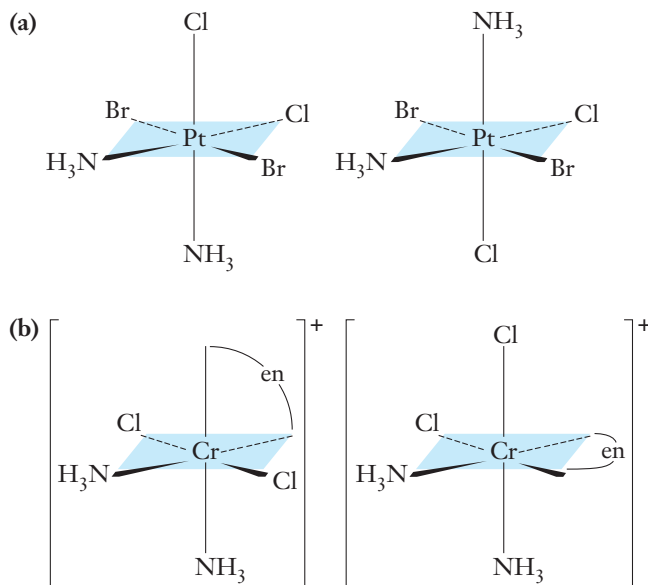
30. Write formulas and provide names for three complex cations in each of the following categories.
 (a) cations coordinated to only monodentate ligands
 (b) cations coordinated to only bidentate ligands
 (c) cations coordinated to two bidentate and two monodentate ligands
 (d) cations coordinated to one tridentate ligand, one bidentate ligand, and one monodentate ligand
 (e) cations coordinated to one tridentate ligand and three monodentate ligands
31. Provide formulas and names for three complex anions that fit each description in Exercise 30.
32. How many geometric isomers can be formed by complexes that are (a) octahedral MA_2B_4 and (b) octahedral MA_3B_3 ? Name any geometric isomers that can exist. Is it possible for any of these isomers to show optical activity (i.e., exist as enantiomers)? Explain.
33. In which of the following complexes are geometric isomers possible? If isomers are possible, draw their structures and label them as *cis* or *trans*, or as *fac* or *mer*.
 (a) $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]^+$
 (b) $[\text{Pt}(\text{NH}_3)_3\text{Br}_3]^-$
 (c) $\text{Co}(\text{NH}_3)_3\text{F}_3$
 (d) $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]^{2+}$

34. Isomers have the same molecular formula. However, it is often important to recognize, identify, or even separate them, especially in the field of medicine. Why?
35. Write the structural formulas for (a) two isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, (b) four isomers (including linkage isomers) of $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$, and (c) two isomers (including ionization isomers) of $[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{Cl}$.



Charles D. Winters
fac isomer of $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$

36. Determine the number and types of isomers that would be possible for each of the following complexes.
- tetraamminediaquachromium(III) ion
 - triaminetrichlorochromium(III)
 - tris(ethylenediamine)chromium(III) ion
 - dichlorobis(ethylenediamine)platinum(IV) chloride
 - diamminedibromodichlorochromate(III) ion
37. Indicate whether the complexes in each pair are identical or isomers. If they are not identical, tell which kind of isomers they represent.



38. Distinguish between constitutional (structural) isomers and stereoisomers.
39. Distinguish between an optically active complex and a racemic mixture.
40. Write the formula for a potential ionization isomer of each of the following compounds. Name each one.
- $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Br}$
 - $[\text{Ni}(\text{en})_2(\text{NO}_2)_2]\text{Cl}_2$
 - $[\text{Fe}(\text{NH}_3)_5\text{CN}]\text{SO}_4$
41. Write the formula for a potential hydrate isomer of each of the following compounds. Name each one.
- $[\text{Cu}(\text{OH}_2)_4]\text{Cl}_2$; (b) $[\text{Ni}(\text{OH}_2)_5\text{Br}]\text{Br} \cdot \text{H}_2\text{O}$
42. Write the formula for a potential coordination isomer of each of the following compounds. Name each one.
- $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$; (b) $[\text{Ni}(\text{en})_3][\text{Cu}(\text{CN})_4]$
43. Write the formula for a potential linkage isomer of each of the following compounds. Name each one.
- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{Cl}$; (b) $[\text{Cr}(\text{NH}_3)_5(\text{CN})](\text{CN})_2$

Crystal Field Theory

44. Describe clearly what Δ_{oct} is. How is Δ_{oct} actually measured experimentally? How is it related to the spectrochemical series?
45. On the basis of the spectrochemical series, determine whether the following octahedral complexes are low spin or high spin.
- $[\text{CrCl}_4\text{Br}_2]^{3-}$
 - $[\text{Co}(\text{en})_3]^{3+}$
 - $[\text{Fe}(\text{OH}_2)_6]^{3+}$
 - $[\text{Fe}(\text{NO}_2)_6]^{3-}$
46. On the basis of the spectrochemical series, determine whether the following octahedral complexes are low spin or high spin.
- $[\text{Cu}(\text{OH}_2)_6]^{2+}$
 - $[\text{MnF}_6]^{3-}$
 - $[\text{Co}(\text{CN})_6]^{3-}$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$



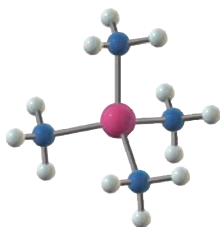
47. Write the electron configuration in t_{2g} and e_g orbitals for each of the following metal ions in an octahedral field.

Metal Ions	Ligand Field Strength
V^{2+}	Weak
Mn^{2+}	Strong
Mn^{2+}	Weak
Ni^{2+}	Weak
Cu^{2+}	Weak
Fe^{3+}	Strong
Cu^+	Weak
Ru^{3+}	Strong

48. Write formulas for two complex ions that would fit into each of the categories of Exercise 47. Name the complex ions you list.
49. Determine the electron configuration of the metal ion in (a) $[Co(CN)_6]^{3-}$, a low spin complex ion; (b) $[CoF_6]^{3-}$, a high spin complex ion; (c) $[Ag(NH_3)_2]^+$, a high spin complex ion; and (d) $[Co(NH_3)_5SO_4]^+$, a low spin complex ion. (e) Which of these complexes is/are paramagnetic? (f) Which is/are diamagnetic?
50. Determine the electron configuration of the metal ion in (a) $[Mn(NH_3)_2(OH_2)_2]^{2+}$, a low spin complex ion; (b) $[Co(NO_2)_6]^{3-}$, a low spin complex ion; (c) $[Cr(NH_3)_4Cl_2]^+$, a low spin complex ion; and (d) $[MnCl_5NO]^{3-}$, a high spin complex ion. (e) Which of these complexes is/are paramagnetic? (f) Which is/are diamagnetic?
51. Identify whether the following complexes are diamagnetic or paramagnetic. If the complex is paramagnetic, further classify it as high spin or low spin and identify the number of unpaired electrons.
- $[Mn(CN)_6]^{4-}$
 - $[Co(NH_3)_6]^{3+}$
 - $Fe(CN)_2(NH_3)_4$
 - $MnCl_2(H_2O)_4$
 - $[Fe(OH)(H_2O)_5]^{2+}$
 - $TiCl_4$
 - $[Co(H_2O)_6]^{2+}$
 - $[Rh(en)_3]^{2+}$

Conceptual Exercises

52. What is the total number of electrons that the cadmium ion, Cd^{2+} , in the tetraamminecadmium(II) ion, $[Cd(NH_3)_4]^{2+}$, shares with the ammonia molecules, NH_3 ?

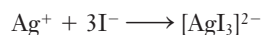


53. Explain why Cr^{2+} forms high-spin and low-spin octahedral complexes, but Cr^{3+} does not.
54. How can you predict whether a complex is high or low spin? How can you determine whether a complex is high or low spin?
55. Define the terms *diamagnetic* and *paramagnetic*. What feature of electronic structure is directly related to these properties?
56. What are three common metal coordination numbers found in coordination chemistry? Give the shape usually associated with each of the common coordination numbers.
57. Several isomers are possible for $[Co(en)(NH_3)(H_2O)_2Cl]^{2+}$. (Two of the isomers have optical isomers.) How many isomers can you draw? Draw the structure of an isomer that does not have an optical isomer. Draw the structure of an isomer that would have an optical isomer. (Hint: "en" is not large enough to bind at *trans* locations.)

Building Your Knowledge

Values of equilibrium constants are listed in Appendix I.

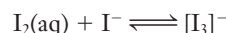
58. Consider the formation of the triiodoargentate(I) ion.



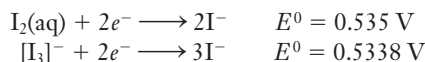
Would you expect an increase or decrease in the entropy of the system as the complex is formed? The standard state absolute entropy at 25°C is 72.68 J/K mol for Ag^+ , 111.3 J/K mol for I^- , and 253.1 J/K mol for $[AgI_3]^{2-}$.

Calculate ΔS° for the reaction and confirm your prediction.

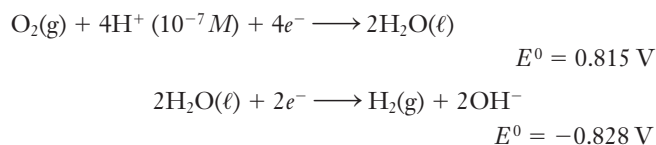
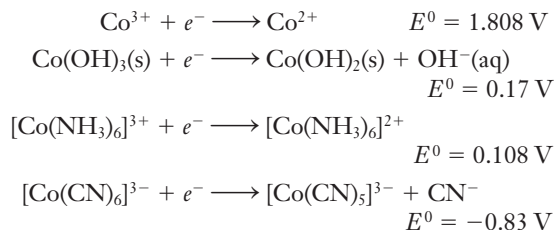
59. Molecular iodine reacts with I^- to form a complex ion.



Calculate the equilibrium constant for this reaction given the following data at 25°C.

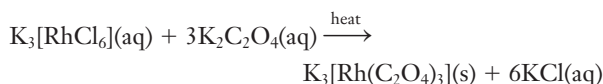


60. Calculate the pH of a solution prepared by dissolving 0.42 mol of tetraamminecopper(II) chloride, $[Cu(NH_3)_4]Cl_2$, in water to give 1.0 L of solution. Ignore hydrolysis of Cu^{2+} .
61. Use the following standard reduction potential data to answer the questions.



Which cobalt(III) species among those listed would oxidize water? Which cobalt(II) species among those listed would be oxidized by water? Explain your answers.

62. For each of the following octahedral complexes, determine (a) the charge of the metal ion, (b) the number of d electrons, (c) low spin or high spin, and (d) the number of unpaired electrons. $[\text{Cr}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{CN})_6]^{4-}$, $[\text{CrF}_6]^{2-}$, $[\text{CoBr}_6]^{4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{4-}$, $[\text{CoF}_6]^{3-}$, $[\text{CuF}_6]^{4-}$, $[\text{MnCl}_6]^{4-}$, $[\text{Mn}(\text{CN})_6]^{4-}$, $[\text{MnF}_6]^{3-}$, $[\text{HgCl}_6]^{4-}$, $[\text{NiF}_6]^{4-}$, and $[\text{TiF}_6]^{3-}$. Then order the complexes by number of d electrons and high or low spin (or both the same). What pattern is there in the number of unpaired electrons for each spin condition?
63. For the low-spin complex $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]\text{ClO}_4$, identify the following:
- the coordination number of cobalt
 - the coordination geometry of cobalt
 - the oxidation number of cobalt
 - the number of unpaired electrons
 - whether the complex is diamagnetic or paramagnetic
- Draw any geometric isomers.
64. Calculate (a) the molar solubility of $\text{Zn}(\text{OH})_2$ in pure water, (b) the molar solubility of $\text{Zn}(\text{OH})_2$ in 0.25 M NaOH solution, and (c) the concentration of $[\text{Zn}(\text{OH})_4]^{2-}$ ions in the solution of (b).
65. The yellow complex oxalatorhodium compound $\text{K}_3[\text{Rh}(\text{C}_2\text{O}_4)_3]$ can be prepared from the wine-red complex compound $\text{K}_3[\text{RhCl}_6]$ by boiling a concentrated aqueous solution of $\text{K}_3[\text{RhCl}_6]$ and $\text{K}_2\text{C}_2\text{O}_4$ for two hours and then evaporating the solution until the product crystallizes.



What is the theoretical yield of the oxalato complex if 1.150 g of the chloro complex is heated with 4.95 g of $\text{K}_2\text{C}_2\text{O}_4$? In an experiment, the actual yield was 0.88 g. What is the percent yield?

Beyond the Textbook

NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.*

66. Use an internet search engine to locate information on chelation therapy. Describe two medical uses of chelation therapy.
67. Use an internet search engine to locate information on chelation in soil. Describe the effects of chelation that result in the improvement of the soil.
68. Use the *Handbook of Chemistry and Physics* or a suitable internet site to find rules and examples of nomenclature of coordination compounds. (a) Give the formulas and names of two anionic ligands that are not listed in this chapter. (b) Give the formula and name of a neutral ligand that is not listed in this chapter. (c) Give the formula of a complex that includes each of these ligands.
69. Technetium complexes are used as radioactive imaging agents in medicine. Look up several Tc-ligand complexes used for this purpose. (a) Compare the ligands and their charges for these complexes. (b) What oxidation states of Tc are in these complexes? (c) What is the most commonly used Tc heart imaging agent?
70. The most “famous” chelating ligand mentioned in this chapter is edta (often capitalized as EDTA). Describe five important uses of EDTA.
71. The Rh complex $[\text{RhI}_2(\text{CO})_2]^-$ is an industrially important catalyst used in what reaction? Prior to 1975 cobalt catalysts were exclusively used for this reaction, but today only Rh catalysts are used even though rhodium is over 1000 times more expensive than cobalt. Why?



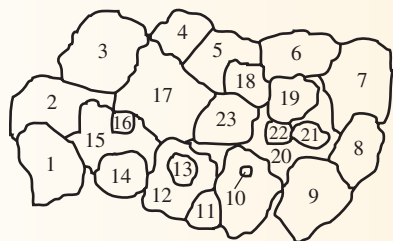
Metals I: Metallurgy

26



A cluster of 21 minerals that are present in ores, plus two samples of native ores (free metals, Ag and Bi). Use the diagram and list of minerals below to identify each sample in the photo.

© 1988 Paul Silverman-Fundamental Photographs



- | | | |
|---|---|--|
| 1. Bornite (iridescent)—COPPER | 10. Vanadinite crystal on Goethite (red crystal)—VANADIUM | 17. Pyrite (gold)—IRON |
| 2. Dolomite (pink)—MAGNESIUM | 11. Cinnabar (red)—MERCURY | 18. Columbite (tan, gray stripe)—NIOBIUM, TANTALUM |
| 3. Molybdenite (gray)—MOLYBDENUM | 12. Galena (gray)—LEAD | 19. Native BISMUTH (shiny) |
| 4. Skutterudite (gray)—COBALT, NICKEL | 13. Monazite (white)—RARE EARTHS: cerium, lanthanum, neodymium, thorium | 20. Rhodochrosite (pink)—MANGANESE |
| 5. Zincite (mottled red)—ZINC | 14. Bauxite (gold)—ALUMINUM | 21. Rutile (shiny twin crystal)—TITANIUM |
| 6. Chromite (gray)—CHROMIUM | 15. Strontianite (white, spiny)—STRONTIUM | 22. Native SILVER (filigree on quartz) |
| 7. Stibnite (top right, gray)—ANTIMONY | 16. Cobaltite (gray cube)—COBALT | 23. Pyrolusite (black, powdery)—MANGANESE |
| 8. Gummite (yellow)—URANIUM | | |
| 9. Cassiterite (rust, bottom right)—TIN | | |

OUTLINE

Metals

26-1 Occurrence of the Metals

Metallurgy

26-2 Pretreatment of Ores

26-3 Reduction to the Free Metals

26-4 Refining of Metals

Metallurgies of Specific Metals

26-5 Magnesium

26-6 Aluminum

26-7 Iron

26-8 Copper

26-9 Gold

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Describe major sources of metals
- ▶ Describe some pretreatment techniques for ores
- ▶ Describe some reduction processes that produce free metals
- ▶ Describe some techniques for refining (purifying) metals
- ▶ Describe the specific metallurgies of five metals: magnesium, aluminum, iron, copper, and gold

Metals

Metals are widely used for structural purposes in buildings, cars, railroads, ships, and aircraft. They also serve as conductors of heat and electricity. During recent decades, medical and nutritional research has provided much insight into important biological functions of metals. The metals Na, K, Ca, and Mg, as well as some nonmetals (C, H, O, N, P, and S), are present in the human body in substantial quantities. Many other metals are present in lesser quantities in the human body, but they are essential to our well-being (see the Chemistry in Use essay “Trace Elements and Life” in Chapter 27). In this chapter, we shall study the occurrence of metals and describe some processes for obtaining metals from their ores.

26-1 Occurrence of the Metals

In our study of periodicity, we learned that metallic character increases toward the left and toward the bottom of the periodic table (see Section 4-10) and that oxides of most metals are basic (see Section 5-9). The oxides of some metals (and metalloids) are amphoteric (see Section 10-6). In Section 13-17 we described metallic bonding and related the effectiveness of metallic bonding to the characteristic properties of metals.

The properties of metals influence the kinds of ores in which they are found and the metallurgical processes used to extract them from their ores. Metals with negative standard reduction potentials (active metals) are found in nature in the combined state. Those with positive reduction potentials (the less active metals) may occur in the uncombined free state as **native ores**. Examples of native ores are Cu, Ag, Au, and the less abundant Pt, Os, Ir, Ru, Rh, and Pd. The first three (Cu, Ag, and Au) are also found in the combined state.

Many insoluble compounds of the metals are found in the earth's crust. Solids that contain these compounds are the **ores** from which metals are extracted. Ores contain **minerals**, which are naturally occurring inorganic solid substances having definite chemical compositions and characteristic crystalline structures. These minerals occur in mixtures with relatively large amounts of **gangue**—sand, soil, rock, and other material. Soluble compounds are found dissolved in the sea or in salt beds in areas where large bodies of water have evaporated. Metal ores can be classified by the anions with which the metal ions are combined (Table 26-1 and Figure 26-1).

▶ Because they have been available in native form throughout history, Cu, Ag, and Au have long been used to produce coins and other valuable objects. Hence they are known as “coinage metals.”

▶ Pronounce “gangue” like “gang,” with only one syllable.

Metallurgy

Metallurgy is the extraction of metals from their ores and the preparation of metals for use. It usually includes several steps: (1) mining the ore, (2) pretreatment of the ore, (3) reduction of the ore to the free metal, (4) refining or purifying the metal, and (5) alloying, if necessary.

Table 26-1 Common Classes of Ores

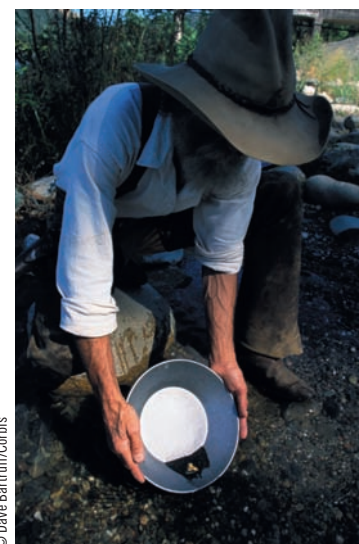
Anion	Examples and Names of Minerals
none (native ores)	Au, Ag, Pt, Os, Ir, Ru, Rh, Pd, As, Sb, Bi, Cu
oxide	hematite, Fe_2O_3 ; magnetite, Fe_3O_4 ; bauxite, Al_2O_3 ; cassiterite, SnO_2 ; periclase, MgO ; silica, SiO_2
sulfide	chalcopryite, CuFeS_2 ; chalcocite, Cu_2S ; sphalerite, ZnS ; galena, PbS ; iron pyrites, FeS_2 ; cinnabar, HgS
chloride	rock salt, NaCl ; sylvite, KCl ; carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
carbonate	limestone, CaCO_3 ; magnesite, MgCO_3 ; dolomite, $\text{MgCO}_3 \cdot \text{CaCO}_3$; rhodochrosite, MnCO_3
sulfate	gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; epsom salts, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; barite, BaSO_4
silicate	beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$; kaolinite, $\text{Al}_2(\text{Si}_2\text{O}_8)(\text{OH})_4$; spodumene, $\text{LiAl}(\text{SiO}_3)_2$

► The most widespread minerals are silicates. But extraction of metals from silicates is very difficult. Metals are obtained from silicate minerals only when there is no other more economical alternative.

26-2 Pretreatment of Ores

After they are mined, many ores must be concentrated by removal of most of the gangue. Most sulfides have relatively high densities and are denser than gangue. After pulverization, the lighter gangue particles are removed by a variety of methods. One involves blowing the lighter particles away via a cyclone separator (Figure 26-2a). These particles can be sifted out through layers of vibrating wire mesh or on inclined vibration tables.

Hydrophilic (“water-loving”) particles are made wet by water; hydrophobic (“water-hating”) particles are not made wet by water. These two kinds of particles are separated in the **flotation process**. This method is particularly applicable to sulfides, carbonates, and silicates, which are not “wetted” by water or which can be made water-repellent by treatment. Their surfaces are easily covered by layers of oil or other flotation agents. A stream of air is blown through a swirled suspension of such an ore in water and oil (or other agent). Bubbles form in the oil on the mineral particles and cause them to rise to the surface. The bubbles are prevented from breaking and escaping by a layer of oil and emulsifying agent. A frothy ore concentrate forms at the surface. By varying the relative amounts of oil and water, the types of oil additive, the air pressure, and other factors, it is even possible to separate one metal sulfide, carbonate, or silicate from another (see Figure 26-2b).



Panning for gold is possible because of the high density of the native metal, which allows it to be separated from less dense rocks and minerals.

KEY									
	Sulfides		Phosphates						
	Oxides		Silicates						
	Occur uncombined		C from coal, B from borax						
	Halide salts		Carbonates						

H																	H	He			
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi			Rn				
Lanthanides																					
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu								

Figure 26-1 Major natural sources of the elements. The soluble halide salts are found in oceans, salt lakes, brine wells, and solid deposits. Most helium is obtained from wells in the United States and Russia. Most of the other noble gases are obtained from air.

Unless otherwise noted, all content on this page is © Cengage Learning.

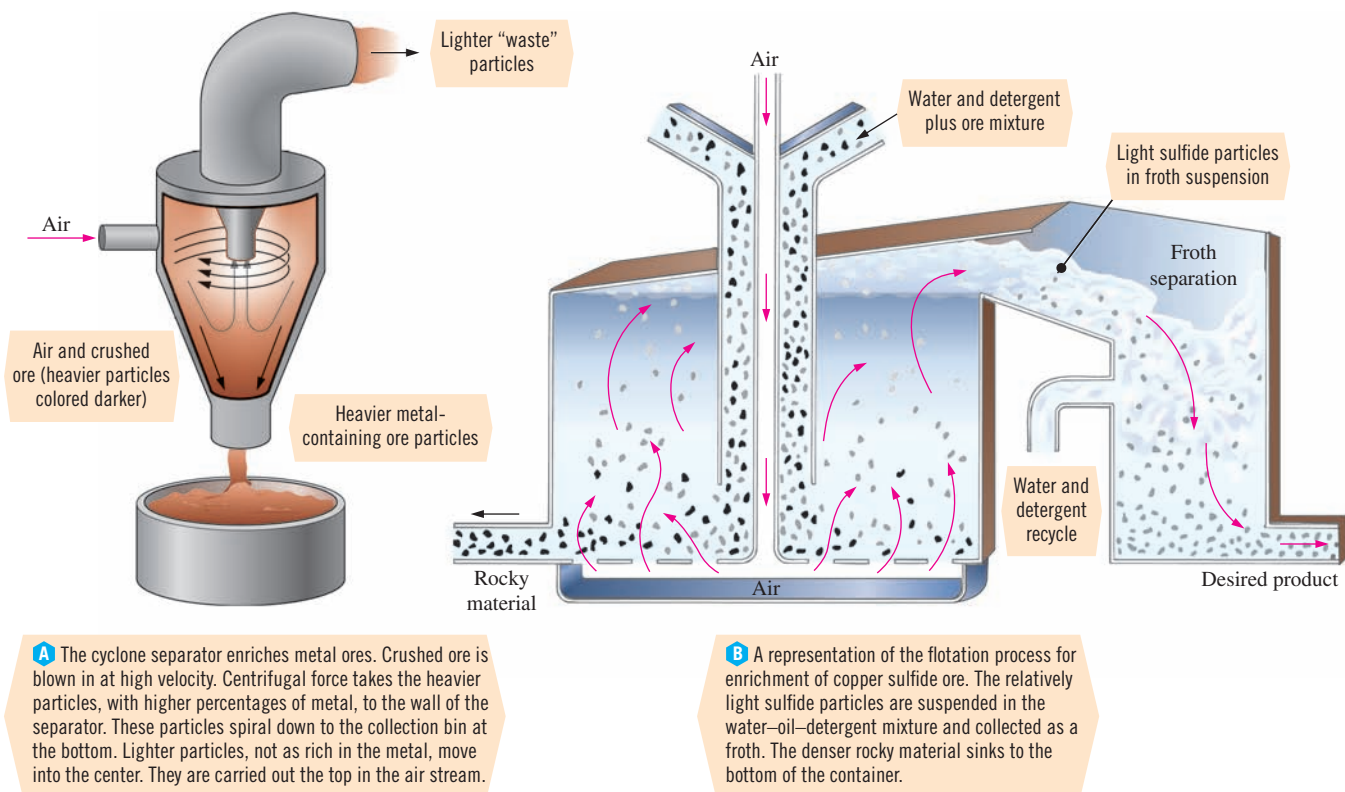
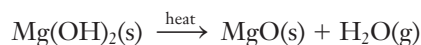
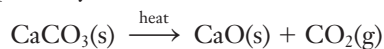
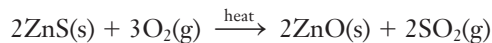


Figure 26-2 Different ways of separating metal ores.

Another pretreatment process involves chemical modification. This converts metal compounds to more easily reduced forms. Carbonates and hydroxides may be heated to drive off CO_2 and H_2O , respectively.



Some sulfides are converted to oxides by **roasting**, that is, heating below their melting points in the presence of oxygen from air. For example,

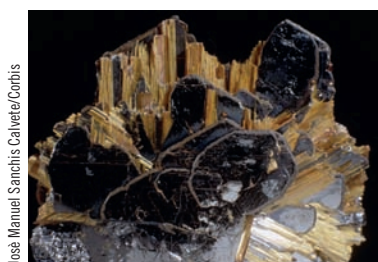


Roasting sulfide ores causes air pollution. Enormous quantities of SO_2 escape into the atmosphere (see Section 6-8), where it causes great environmental damage (Figure 26-3). Federal regulations now require limitation of the amount of SO_2 that escapes with stack gases and fuel gases. Now most of the SO_2 is trapped and used in the manufacture of sulfuric acid (see Section 28-12).



Charles D. Winters

Some sulfide minerals: iron pyrite (fool's gold), FeS_2 ; black galena, PbS ; yellow orpiment, As_2S_3 .



Jose Manuel Sanchis Calvet/Corbis

Rutile, appearing here as thin tan crystals and thicker black ones, is TiO_2 .

Figure 26-3 Sulfur dioxide, $\text{SO}_2(\text{g})$, that escapes from the roasting of sulfide ores (or the burning of coal in power plants) reacts with water in the atmosphere to form acid rain. This can seriously damage trees as shown in this photo from the southwestern United States.

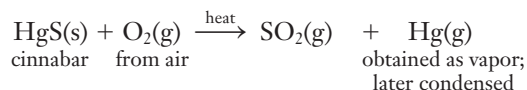


© Ray Pforntner/Ray Pforntner.com

26-3 Reduction to the Free Metals

The method used for reduction of metals from their compounds in ores to the free metals depends on how strongly the metal ions are bonded to anions. When the bonding is strong, more energy is required to reduce the metals. This makes reduction more expensive. The most active metals usually have the strongest bonding.

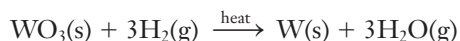
The least reactive metals occur in the free state and thus require no reduction. Examples include Au, Ag, and Pt. This is why gold and silver have been used as free metals since pre-historic times. Some less active metals, such as Hg, can be obtained directly from their sulfide ores by roasting. This reduces metal ions to the free metals by oxidation of the sulfide ions to form SO₂ gas.



Roasting sulfides of the more active metals produces metal oxides, but no free metals.



In a process called **smelting**, the resulting metal oxides are then reduced to free metals with coke (impure carbon), CO, or another reducing agent, such as H₂, Fe, or Al.



The very active metals, such as Al and Na, are reduced electrochemically, usually from their anhydrous molten salts. If H₂O is present, it is reduced instead of the more active metals. Tables 26-2 and 26-3 summarize reduction processes for some metal ions.

► Can you use oxidation states (Chapter 5) to show which elements are oxidized and which ones are reduced?

Table 26-2 Reduction Processes for Some Metals

	Metal Ion	Typical Reduction Process
Increasing activity of metals ↑	lithium, Li ⁺	Electrolysis of molten salt
	potassium, K ⁺	
	calcium, Ca ²⁺	
	sodium, Na ⁺	
	magnesium, Mg ²⁺	
	aluminum, Al ³⁺	
	manganese, Mn ²⁺	Reaction of oxide with coke (carbon) or carbon monoxide (CO)
	zinc, Zn ²⁺	
	chromium, Cr ²⁺ , Cr ³⁺	
	iron, Fe ²⁺ , Fe ³⁺	
	lead, Pb ²⁺	Element occurring free, or easily obtained by roasting the sulfide or oxide ore
	copper, Cu ²⁺	
	silver, Ag ⁺	
	mercury, Hg ²⁺	
	platinum, Pt ²⁺	
	gold, Au ⁺	



The mineral rhodochrosite is manganese carbonate, MnCO₃.

Table 26-3 Some Specific Reduction Processes

Metal	Compound (ore)	Reduction Process	Comments
mercury	HgS (cinnabar)	Roast reduction; heating of ore in air $\text{HgS} + \text{O}_2 \xrightarrow{\text{heat}} \text{Hg} + \text{SO}_2$	
copper	sulfides such as Cu_2S (chalcocite)	Blowing of oxygen through purified molten Cu_2S $\text{Cu}_2\text{S} + \text{O}_2 \xrightarrow{\text{heat}} 2\text{Cu} + \text{SO}_2$	Preliminary ore concentration and purification steps required to remove FeS impurities
zinc	ZnS (sphalerite)	Conversion to oxide and reduction with carbon $2\text{ZnS} + 3\text{O}_2 \xrightarrow{\text{heat}} 2\text{ZnO} + 2\text{SO}_2$ $\text{ZnO} + \text{C} \xrightarrow{\text{heat}} \text{Zn} + \text{CO}$	Process also used for the production of lead from galena, PbS
iron	Fe_2O_3 (hematite)	Reduction with carbon monoxide produced from coke $2\text{C (coke)} + \text{O}_2 \xrightarrow{\text{heat}} 2\text{CO}$ $\text{Fe}_2\text{O}_3 + 3\text{CO} \xrightarrow{\text{heat}} 2\text{Fe} + 3\text{CO}_2$	
titanium	TiO_2 (rutile)	Conversion of oxide to halide salt and reduction with an active metal $\text{TiO}_2 + 2\text{Cl}_2 + 2\text{C} \xrightarrow{\text{heat}} \text{TiCl}_4 + 2\text{CO}$ $\text{TiCl}_4 + 2\text{Mg} \xrightarrow{\text{heat}} \text{Ti} + 2\text{MgCl}_2$	Also used for the reduction of UF_4 obtained from UO_2 , pitchblende
tungsten	FeWO_4 (wolframite)	Reduction with hydrogen $\text{WO}_3 + 3\text{H}_2 \xrightarrow{\text{heat}} \text{W} + 3\text{H}_2\text{O}$	Used also for molybdenum
aluminum	$\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (bauxite)	Electrolytic reduction (electrolysis) in molten cryolite, $\text{Na}_3[\text{AlF}_6]$, at $\approx 1000^\circ\text{C}$ $2\text{Al}_2\text{O}_3 \longrightarrow 4\text{Al} + 3\text{O}_2$	
sodium	NaCl (seawater)	Electrolysis of molten chlorides $2\text{NaCl} \longrightarrow 2\text{Na} + \text{Cl}_2$	Also for calcium, magnesium, and other active metals in Groups 1A and 2A

26-4 Refining of Metals

Metals obtained from reduction processes are almost always impure. Further **refining** (purification) is usually required. This can be accomplished by distillation if the metal is more volatile than its impurities, as in the case of mercury. Among the metals purified by electrolysis (see Sections 21-3 to 21-7) are Al (Section 26-6), Cu (Section 26-8), Ag, and Au (Section 26-9).

Zone refining is often used when extremely pure metals are desired for such applications as solar cells and semiconductors (see Section 13-17). An induction heater surrounds a bar of the impure solid and passes slowly from one end to the other (Figure 26-4). As it passes, it melts successive portions of the bar, which then slowly recrystallize as the heating element moves away. The impurity does not fit into the metallic crystal as easily as the element of interest, so most of it is carried along in the molten portion until it reaches the end. Repeated passes of the heating element produce a bar of high purity. The end containing the impurities can be sliced off and recycled.

After the refining, many metals are alloyed, or mixed with other elements, to change their physical or chemical characteristics. In some cases, certain impurities are allowed to remain during refining because their presence improves the properties of the metal. For example, a small amount of carbon in iron greatly enhances its hardness. Examples of alloys include brass (Cu and Zn), bronze (Cu and Sn), duralumin (Al, Cu, Mg, and Mn), and stainless steel (Fe, Cr, Ni, and others).

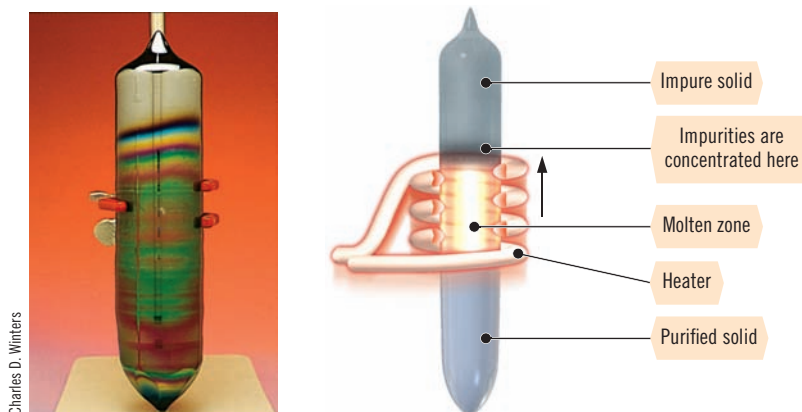


Figure 26-4 Ultrapure silicon is produced by zone refining as shown in the schematic at right.

Metallurgies of Specific Metals

The metallurgies of Mg, Al, Fe, Cu, and Au will be discussed as specific examples. The order of increasing standard reduction potentials of these metals indicates the order of increasing ease of reduction to the free metals.

► Mg and Al are active metals, Fe and Cu are moderately active, and Au is relatively inactive.

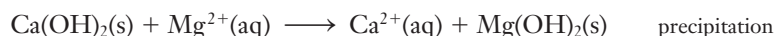
Reduction Half-Reaction	Standard Reduction Potential E^0 , Volts
$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	-2.37
$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$	-1.66
$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	-0.44
$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	+0.337
$\text{Au}^{3+} + 3e^- \longrightarrow \text{Au}$	+1.50



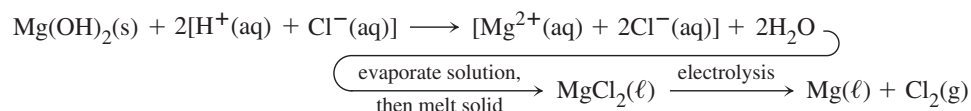
26-5 Magnesium

Because of its low density (1.74 g/cm³), magnesium is used in lightweight structural alloys for such items as automobile and aircraft parts. Magnesium occurs widely in carbonate ores, but most Mg comes from salt brines and from the sea (Figure 26-5). Seawater is 0.13% Mg by mass.

Magnesium ions are precipitated as Mg(OH)₂ by addition of Ca(OH)₂ (slaked lime) to seawater. The slaked lime is obtained by crushing oyster shells (CaCO₃), heating them to produce lime (CaO), and then adding a limited amount of water (slaking).



The third reaction occurs because K_{sp} for Mg(OH)₂, 1.5×10^{-11} , is much smaller than that for Ca(OH)₂, 7.9×10^{-6} . The milky white suspension of Mg(OH)₂ is filtered, and the solid Mg(OH)₂ is then neutralized with HCl to produce a MgCl₂ solution. Evaporation of the H₂O leaves solid MgCl₂, which is then melted and electrolyzed (Figure 26-6) under an inert atmosphere to produce molten Mg and gaseous Cl₂. The products are separated as they are formed, to prevent recombination.



Oyster shells are mainly composed of CaCO₃.

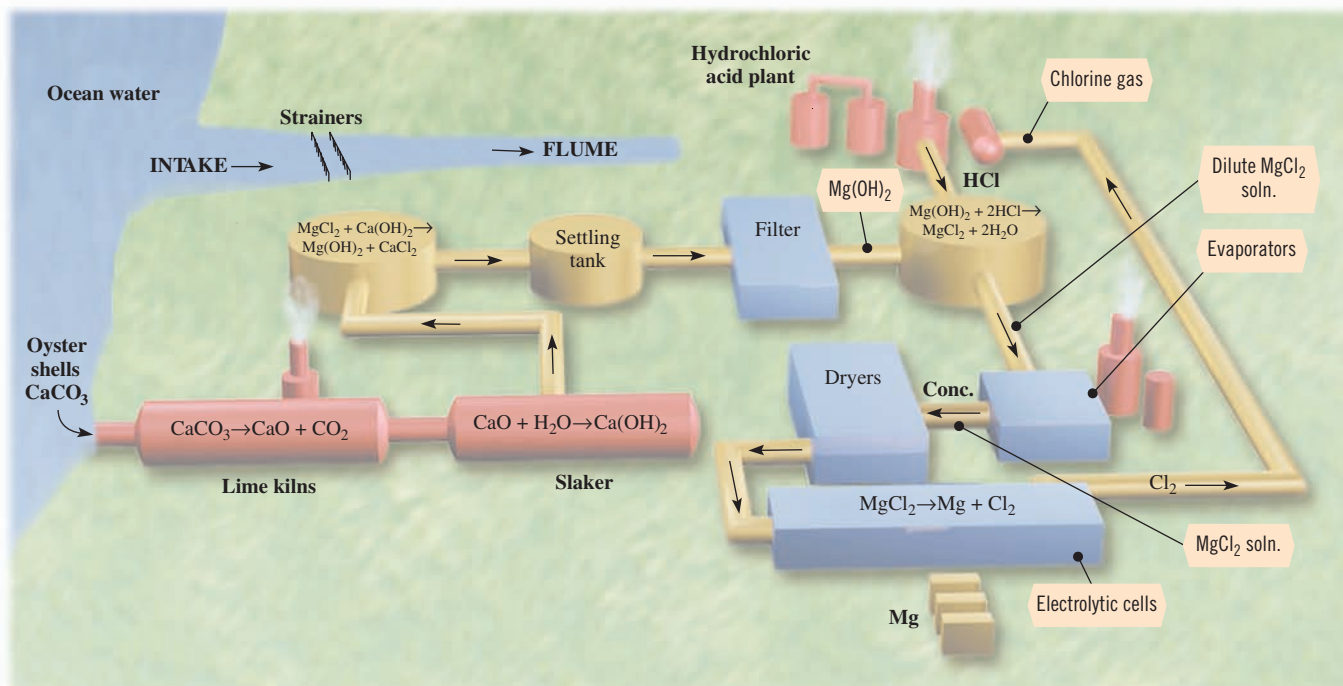


Figure 26-5 Schematic diagram of an industrial plant for the production of magnesium from the Mg^{2+} ions in seawater.

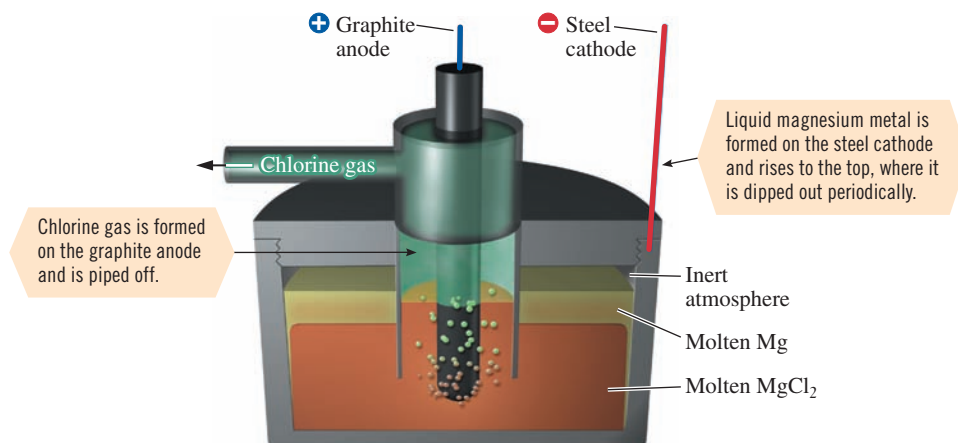


Figure 26-6 A cell for electrolyzing molten MgCl_2 . The magnesium metal is formed on the steel cathode and rises to the top, where it is dipped off periodically. Chlorine gas is formed around the graphite anode and is piped off.

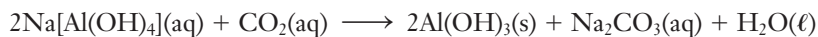
Magnesium is cast into ingots or alloyed with other light metals. The Cl_2 byproduct is used to produce more HCl for neutralization of Mg(OH)_2 .

26-6 Aluminum

► Recall that Al_2O_3 is amphoteric. Impurities such as oxides of iron, which are not amphoteric, are left behind in the crude ore.

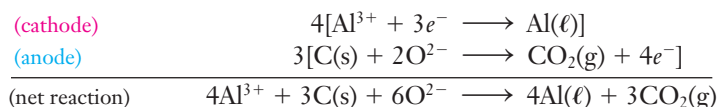
Aluminum is the most commercially important nonferrous metal. Its chemistry and uses will be discussed in Section 27-7. Aluminum is obtained from bauxite, or hydrated aluminum oxide, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. Aluminum ions can be reduced to Al by electrolysis only in the absence of H_2O . First the crushed bauxite is purified by dissolving it in a concentrated solution of sodium hydroxide, NaOH , to form soluble $\text{Na[Al(OH)}_4]$. Then $\text{Al(OH)}_3 \cdot x\text{H}_2\text{O}$ is precipitated from the filtered solution by blowing in carbon dioxide to neutralize the

unreacted NaOH and one OH⁻ ion per formula unit of Na[Al(OH)₄]. Heating the hydrated product dehydrates it to Al₂O₃.



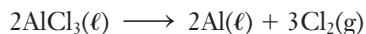
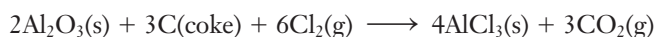
The melting point of Al₂O₃ is 2045°C; electrolysis of pure molten Al₂O₃ would have to be carried out at or above this temperature, with great expense. In some metallurgical processes, another substance is added to react with (or to dissolve) the charge or a product of the reduction. Such an additive is called a **flux**. When the lower-melting mineral cryolite (Na₃[AlF₆], mp 1012°C) is added as a flux in this process, the Al₂O₃ dissolves in molten cryolite at a much lower temperature. The molten mixture can then be electrolyzed at 1000°C with carbon electrodes. The cell used industrially for this process, called the **Hall–Héroult process**, is shown in Figure 26-7.

The inner surface of the cell is coated with carbon or carbonized iron, which functions as the cathode at which aluminum ions are reduced to the free metal. The graphite anode is oxidized to CO₂ gas and must be replaced frequently. This is one of the chief costs of aluminum production.



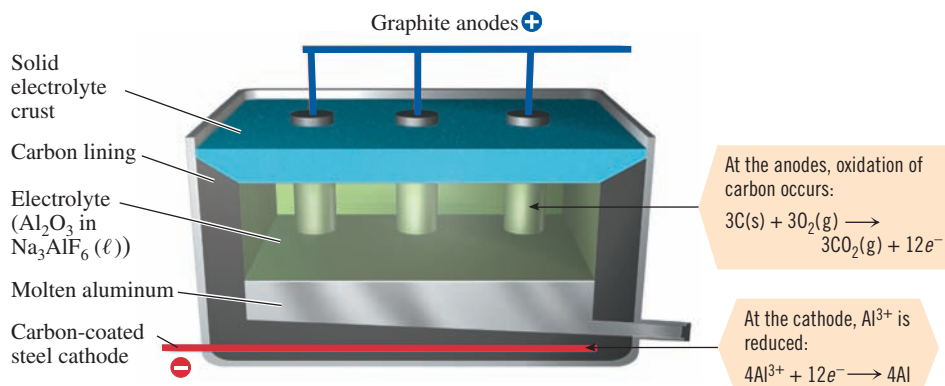
Molten aluminum is denser than molten cryolite, so it collects in the bottom of the cell and is drawn off and cooled to a solid.

A more economical approach, the Alcoa chlorine process, has now been developed on a commercial scale. The anhydrous bauxite is first converted to AlCl₃ by reaction with Cl₂ in the presence of carbon. The AlCl₃ is then melted and electrolyzed to give aluminum, and the recovered chlorine is reused in the first step.



This process uses only about 60% as much electrical energy as the Hall–Héroult process.

The use of large amounts of electrical energy in electrolysis makes production of aluminum from ores an expensive metallurgy. Methods for recycling used Al use less than 10% of the energy required to make new metal from bauxite by the Hall–Héroult process. Processing of recycled Al now accounts for more than half of the production of this metal.



A Schematic drawing of a cell for producing aluminum by electrolysis of a melt of Al₂O₃ in cryolite, Na₃[AlF₆]. The molten aluminum collects in the container, which acts as the cathode.

► For clarity, we have not shown waters of hydration.

► A mixture of compounds typically has a lower melting point than any of the pure compounds (see Chapter 14).



Many consumer items are made of aluminum.



B Casting molten aluminum. Electrolytic cells used in the Hall–Héroult process appear in the background.

Figure 26-7 Electrolytic production of aluminum metal.

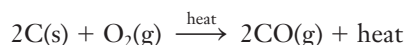
Unless otherwise noted, all content on this page is © Cengage Learning.

Recycling of aluminum drink cans is now so successful that more than two-thirds of this aluminum is used to produce new cans. The typical time elapsed from collection of cans until new ones made from the same aluminum appear on supermarket shelves is only a few weeks.

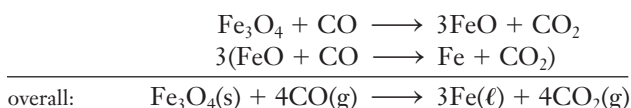
26-7 Iron

► In Fe_3O_4 , the formal oxidation state of iron is $+\frac{8}{3}$. Two-thirds of the Fe atoms are in the +3 state and the other one-third are in the +2 state. The formula is sometimes written as $\text{Fe}_2\text{O}_3 \cdot \text{FeO}$.

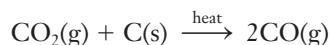
The most desirable iron ores contain hematite, Fe_2O_3 , or magnetite, Fe_3O_4 . As the available supplies of these high-grade ores have dwindled, taconite, which is magnetite in very hard silica rock, has become an important source of iron. The oxide is reduced in blast furnaces (Figure 26-8) by carbon monoxide. Coke mixed with limestone (CaCO_3) and crushed ore is admitted at the top of the furnace as the *charge*. A blast of hot air from the bottom burns the coke to carbon monoxide with the evolution of more heat.



Most of the oxide is reduced to molten iron by carbon monoxide, although some is reduced directly by coke. Several stepwise reductions occur (see Figure 26-8), but the main reactions for Fe_3O_4 can be summarized as follows:



Much of the CO_2 reacts with excess coke to produce more CO to reduce the next incoming charge.



© Stephanie Maze/Corbis

Iron ore is scooped in an open-pit mine.

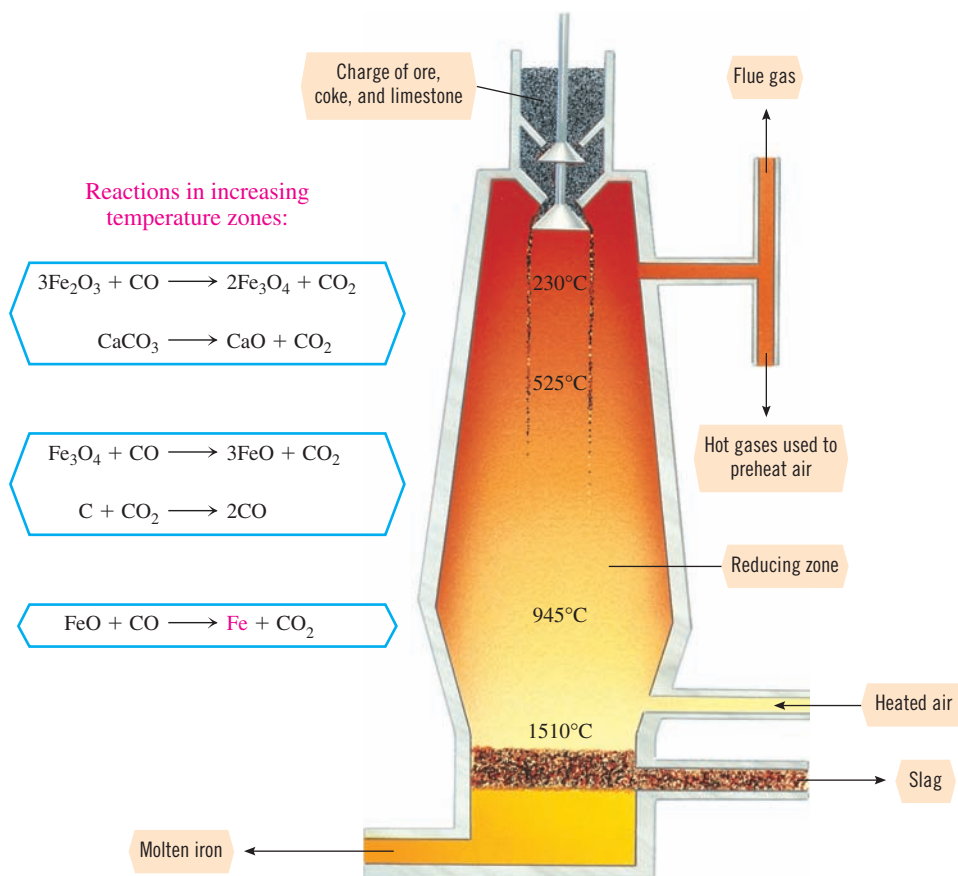
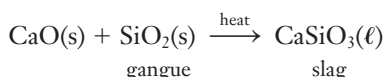
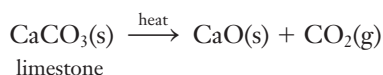


Figure 26-8 A schematic drawing of a blast furnace for reduction of iron ore.

Unless otherwise noted, all content on this page is © Cengage Learning.

The limestone, acting as a flux, reacts with the silica gangue in the ore to form a molten **slag** of calcium silicate.



The slag is less dense than molten iron; it floats on the surface of the iron and protects it from atmospheric oxidation. Both are drawn off periodically. Some of the slag is subsequently used in the manufacture of cement.

The iron obtained from the blast furnace contains carbon, among other things. It is called **pig iron**. If it is remelted, run into molds, and cooled, it becomes **cast iron**. This is brittle because it contains much iron carbide, Fe_3C . If all the carbon is removed, nearly pure iron can be produced. It is silvery in appearance, quite soft, and of little use. If *some* of the carbon is removed and other metals such as Mn, Cr, Ni, W, Mo, and V are added, the mixture becomes stronger and is known as **steel**. There are many types of steel, containing alloyed metals and other elements in various controlled proportions (Table 26-4). Stainless steels show high tensile strength and excellent resistance to corrosion. The most common kind contains 14–18% chromium and 7–9% nickel.

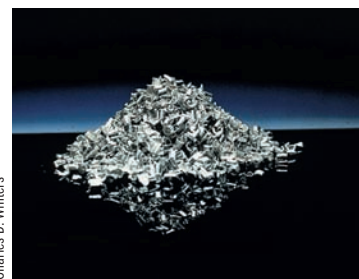
Pig iron can also be converted to steel by burning out most of the carbon with O_2 in a basic oxygen furnace (Figure 26-9). Oxygen is blown through a heat-resistant tube inserted below the surface of the *molten* iron. Carbon burns to CO, which subsequently escapes and burns to CO_2 .

► Reaction of a metal oxide (basic) with a nonmetal oxide (acidic) forms a salt.

► Considerable amounts of slag are also used to neutralize acidic soil. If there were no use for the slag, its disposal would be a serious economical and environmental problem.

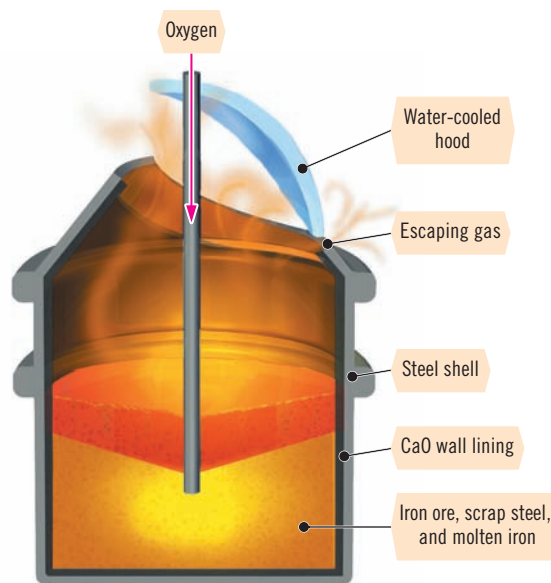
Table 26-4 Some Steels and Their Uses

Name	Composition	Properties	Uses
carbon steel	1.3% C, 98.7% Fe	hard	sheet steel, tools
manganese steel	10–18% Mn, 90–82% Fe, 0.5% C	hard, resistant to wear	railroad rails, safes, armor plate
stainless steel	14–18% Cr, 7–9% Ni, 79–73% Fe, 0.2% C	resistant to corrosion	cutlery, instruments
nickel steel	2–4% Ni, 98–96% Fe, 0.5% C	hard, elastic, resistant to corrosion	drive shafts, gears, cables
invar steel	36% Ni, 64% Fe, 0.5% C	low coefficient of expansion	meter scales, measuring tapes
silicon steel	1–5% Si, 99–95% Fe, 0.5% C	hard, strong, highly magnetic	magnets
duriron	12–15% Si, 88–85% Fe, 0.85% C	resistant to corrosion by acids	pipes
high-speed steel	14–20% W, 86–80% Fe, 0.5% C	retains temper when hot	high-speed cutting tools



Charles D. Winters

A pile of manganese metal. Manganese is an important element in steels that must withstand great shock, such as those used to construct rock crushers.



© Photo Alto/Getty

A Much of the steel manufactured today is refined by blowing oxygen through a furnace that is charged with scrap and molten iron from a blast furnace.

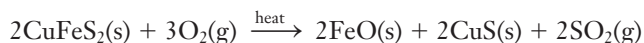
B After the refined iron is withdrawn into a ladle, alloying elements are added to produce the desired steel. The steel industry is one of the nation's largest consumers of oxygen.

Figure 26-9 A representation of the basic oxygen process furnace.

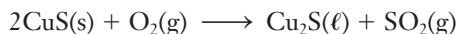
26-8 Copper

Copper is widely used, especially in its alloys such as bronze (Cu and Sn) and brass (Cu and Zn). As a result, it is becoming very scarce and its cost has increased greatly in recent years. The U.S. Bureau of Mines estimates that the known worldwide reserves of copper ore will be exhausted during the first half of the 21st century (Figure 26-10). It is now profitable to mine ores containing as little as 0.25% copper. The increased use of fiber optics in place of copper in communications cables may help to lessen the demand for this metal. The use of superconducting materials in electricity transmission lines could eventually provide enormous savings.

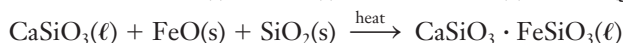
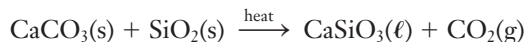
The two main classes of copper ores are the mixed sulfides of copper and iron—such as chalcopyrite, CuFeS_2 —and the basic carbonates—such as azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, and malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$. Let's consider CuFeS_2 (or $\text{CuS} \cdot \text{FeS}$). The copper compound is separated from gangue by flotation (Figures 26-2b and 26-11) and then roasted to remove volatile impurities. Enough air is used to convert iron(II) sulfide, but not copper(II) sulfide, to the oxide.



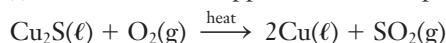
The roasted ore is then mixed with sand (SiO_2), crushed limestone (CaCO_3), and some unroasted ore that contains copper(II) sulfide in a reverberatory furnace at 1100°C . CuS is reduced to Cu_2S , which melts.



The limestone and silica form a molten calcium silicate glass. This dissolves iron(II) oxide to form a slag less dense than the molten copper(I) sulfide, on which it floats.

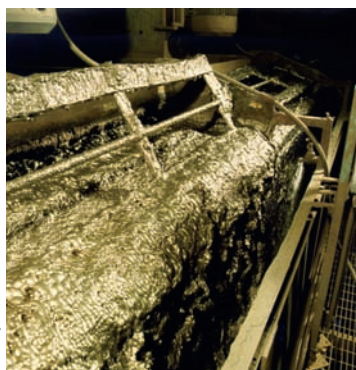


The slag is periodically drained off. The molten copper(I) sulfide is drawn off into a Bessemer converter, where it is again heated and treated with air. This oxidizes sulfide ions to SO_2 and reduces copper(I) ions to metallic copper. The overall process is



James Cowlin

Figure 26-10 An open-pit copper mine near Bagdad, Arizona.



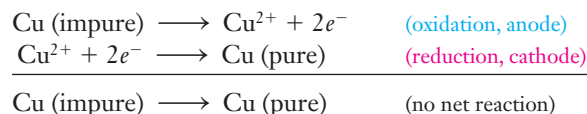
Courtesy of ASARCO LLC

Figure 26-11 A copper ore being enriched by flotation.

► The steps of this process are described in Exercise 48 at the end of the chapter.

Unless otherwise noted, all content on this page is © Cengage Learning.

The impure copper is refined using an electrolytic cell such as the one shown in Figure 26-12. Thin sheets of very pure copper are made to act as cathodes by connecting them to the negative terminal of a dc generator. Chunks of impure copper connected to the positive terminal function as anodes. The electrodes are immersed in a solution of copper(II) sulfate and sulfuric acid. When the cell operates, Cu from the impure anodes is oxidized and goes into solution as Cu^{2+} ions; Cu^{2+} ions from the solution are reduced and the product plates out as metallic Cu on the pure Cu cathodes. Other active metals from the impure bars also go into solution after oxidation. They do not plate out onto the cathode bars of pure Cu because of the far greater concentration of the more easily reduced Cu^{2+} ions that are already in solution. Overall, there is no net reaction, but merely a simultaneous transfer of Cu from anode to solution and from solution to cathode.



Nevertheless, the net effect is that small bars of very pure Cu and large bars of impure Cu are converted into large bars of very pure Cu and small bars of impure Cu.

26-9 Gold

Gold is an inactive metal (sometimes called a noble metal), so it occurs mostly in the native uncombined state. It is sometimes found as gold telluride. Because of its high density, metallic gold can be concentrated by *panning*. In this operation, gold-bearing sand and gravel are gently swirled with water in a pan. The lighter particles spill over the edge, and the denser nuggets of gold remain. Gold is concentrated by sifting crushed gravel in a stream of water on a slightly inclined shaking table that contains several low barriers. These impede the descent of the heavier gold particles, but allow the lighter particles to pass over. In a modern extension to this centuries-old process, the gold is then alloyed with mercury and removed. The mercury is distilled away, leaving behind the pure gold.

Gold is also recovered from the anode sludge from electrolytic purification of copper. Gold is so rare that it is also obtained from very low grade ores by the cyanide process. Air is bubbled through an agitated slurry of the ore mixed with a solution of NaCN. This causes slow oxidation of the metal and the formation of a soluble complex compound.

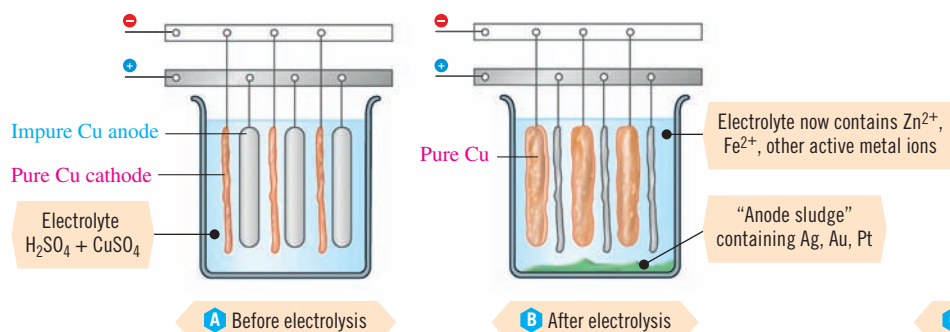
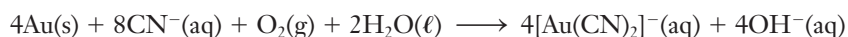
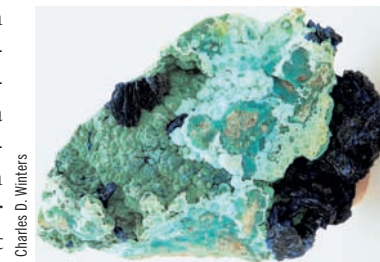
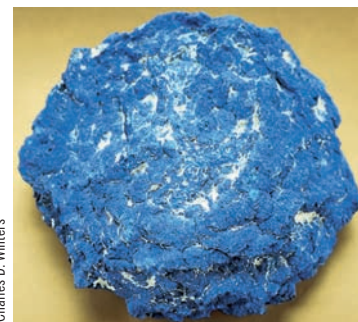


Figure 26-12 A schematic diagram of the electrolytic cell used for refining copper.



Charles D. Winters

A Malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$ or $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, is green.



Charles D. Winters

B Azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ or $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, is blue.

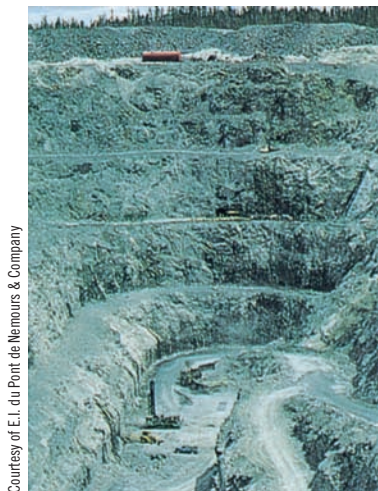
Two copper-containing minerals.

► A sludge called anode mud collects under the anodes. It contains such valuable and difficult-to-oxidize elements as Au, Pt, Ag, Se, and Te. The separation, purification, and sale of these elements reduce the cost of refined copper.



Cheryl Ravelo/Reuters/Corbis

C Commercial electrolysis cells for refining copper



Courtesy of E.I. du Pont de Nemours & Company

Mining low-gold ore in an open-pit mine.

After filtration, free gold can then be regenerated by electrolytic reduction or by reduction of $[\text{Au}(\text{CN})_2]^-$ with zinc.



Because of environmental concerns about mercury toxicity, the cyanide process is increasingly preferred. This is not to suggest that mercury is more toxic than cyanide. The problems due to mercury are greater in that it persists in the environment for a long time, and mercury poisoning is cumulative.

KEY TERMS

Alloying Mixing of a metal with other substances (usually other metals) to modify its properties.

Cast iron The brittle iron obtained when the pig iron from the blast furnace is remelted, run into molds, and cooled; contains much iron carbide, Fe_3C .

Charge (in metallurgy) A sample of crushed ore as it is admitted to a furnace for smelting.

Flotation A method by which hydrophobic (water-repelling) particles of an ore are separated from hydrophilic (water-attracting) particles in a metallurgical pretreatment process.

Flux A substance added to react with or dissolve the charge, or a product of its reduction, in metallurgy; usually added to lower a melting point.

Gangue Sand, rock, and other impurities present with the mineral of interest in an ore.

Hall-Héroult process A process in which a molten mixture of Al_2O_3 , NaF , and AlF_3 is electrolyzed to obtain pure aluminum.

Metallurgy The overall processes by which metals are extracted from ores.

Mineral A naturally occurring inorganic solid substance having a definite chemical composition and characteristic crystalline structure.

Native ore A metal that occurs in an uncombined or free state in nature.

Ore A natural deposit containing a mineral of an element to be extracted.

Pig iron The iron obtained from the blast furnace.

Refining Purifying of a substance.

Roasting Heating a compound below its melting point in the presence of air.

Slag Unwanted material produced during smelting.

Smelting Chemical reduction of a metal from its ore by treating the molten ore with a reducing agent.

Steel Iron alloyed with other metals, such as Mn, Cr, Ni, W, Mo, and V, and sometimes with C and Si.

Zone refining A method of purifying a bar of metal by passing it through an induction heater; this causes impurities to move along in the melted portion.

EXERCISES

Molecular Reasoning exercises

More Challenging exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

General Concepts

- List the chemical and physical properties that we usually associate with metals.
- Define the term “metallurgy.” What does the study of metallurgy include?
- Define the terms (a) gangue, and (b) slag.

- Briefly describe one method by which gangue can be separated from the desired mineral during the concentration of an ore.
- What kinds of metals are most apt to occur in the uncombined (native) state in nature?
- Most of the methods used for collecting and concentrating gold make use of which one of its properties?

Molecular Reasoning exercises

More Challenging exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

7. How does an ore differ from a mineral? Name the three general categories of procedures needed to produce pure metals from ores. Describe the purpose of each.
8. List the six anions (and their formulas) that are most often combined with metals in ores. Give at least one example of an ore of each kind. Which anion is the most commonly encountered?
9. Give the five general steps involved in extracting a metal from its ore and converting the metal to a useful form. Briefly describe the importance of each.
10. Describe the flotation method of ore pretreatment. Are any chemical changes involved?
11. Smelting is the process by which a metal ore is reduced. In this context, what does the term “reduced” mean?
12. Which metals are likely to be found in the free state in nature? Why are these metals in the free state in nature? Describe the location of these elements on the periodic table. Is there a pattern?
13. What kinds of ores are roasted? What kinds of compounds are converted to oxides by roasting? What kinds are converted directly to the free metals?
14. Of the following compounds, which would you expect to require electrolysis to obtain the free metals: KCl ; $\text{Cr}_2(\text{SO}_4)_3$; Fe_2O_3 ; Al_2O_3 ; Ag_2S ; MgSO_4 ? Why?
15. At which electrode is the free metal produced in the electrolysis of a metal compound? Why?
16. Write the equation that describes the electrolysis of a brine solution to form NaOH , Cl_2 , and H_2 . What mass of each substance will be produced in an electrolysis cell for each mole of electrons passed through the cell? Assume 100% efficiency.
17. The following equations represent reactions used in some important metallurgical processes.
 - (a) $\text{Fe}_3\text{O}_4(\text{s}) + \text{CO}(\text{g}) \longrightarrow \text{Fe}(\ell) + \text{CO}_2(\text{g})$
 - (b) $\text{MgCO}_3(\text{s}) + \text{SiO}_2(\text{s}) \longrightarrow \text{MgSiO}_3(\ell) + \text{CO}_2(\text{g})$
 - (c) $\text{Au}(\text{s}) + \text{CN}^- + \text{H}_2\text{O}(\ell) + \text{O}_2(\text{g}) \longrightarrow [\text{Au}(\text{CN})_2]^- + \text{OH}^-$
 Balance the equations. Which one(s) represent reduction to a free metal?
18. Why are cast iron and steel used a lot more than pure iron?
19. What property of many sulfides, carbonates, and silicates allows them to be separated from gangue by the flotation process?
20. Repeat Exercise 17 for
 - (a) Al_2O_3 (cryolite solution) $\xrightarrow{\text{electrolysis}}$ $\text{Al}(\ell) + \text{O}_2(\text{g})$
 - (b) $\text{PbSO}_4(\text{s}) + \text{PbS}(\text{s}) \longrightarrow \text{Pb}(\ell) + \text{SO}_2(\text{g})$
 - (c) $\text{TaCl}_5(\text{g}) + \text{Mg}(\ell) \longrightarrow \text{Ta}(\text{s}) + \text{MgCl}_2(\ell)$

21. Suggest a method of obtaining manganese from an ore containing manganese(III) oxide, Mn_2O_3 . On what basis do you make the suggestion?



Manganese(IV) oxide nodules are recovered from the seafloor.

22. What is the purpose of utilizing the basic oxygen furnace after the blast furnace in the production of iron?
23. A blast furnace utilizes or produces five species that include carbon. (a) List the five species that contain carbon. (b) Explain the function of each step in the chain of events from heating the ore to the production of steel.
24. Magnesium hydroxide can be precipitated from seawater by adding slaked lime, $\text{Ca}(\text{OH})_2$. (a) Why does this precipitation occur? (b) Could this process be used to remove sodium from seawater? Why?
25. Describe the metallurgy of (a) copper and (b) magnesium.
26. Describe the metallurgy of (a) iron and (b) gold.



Native gold

27. Briefly describe the Hall–Héroult process for the commercial preparation of aluminum.
28. (a) Compare the refining of aluminum by the Hall–Héroult process and by the Alcoa chlorine process. (b) Which process is less expensive and why? (c) The Alcoa chlorine process is potentially more dangerous to the workers than is the Hall–Héroult process. Why?
29. Because brass is a mixture of metals, its composition can vary. Common brass is 37% zinc. However, special kinds of brass may contain tin, aluminum, arsenic, lead, or different percentages of zinc (from 5% to 50%) to give them particular properties. Besides zinc, what one metal do all types of brass contain?



30. Disadvantages of the Hall–Héroult process for the electrolytic production of aluminum include the large amount of electricity required, the high temperature needed, and the cost of frequently replacing the graphite anodes, which are oxidized in the process. What advantage or advantages would the Alcoa chlorine process appear to have, compared with the Hall–Héroult process?
31. A common iron ore is magnetite, Fe_3O_4 . In this formula for magnetite, the oxidation number of iron is not an integer. Write the formula in a form that includes only integer oxidation numbers.
32. Name some common minerals that contain iron. Write the chemical formula for the iron compound in each. What is the oxidation number of iron in each substance?
33. ● What is steel? How does the hardness of iron compare with that of steel?
34. ● (a) What is the difference in composition between pure iron and steel? (b) What is the name of the process by which steel is produced?
35. Noble metals, such as Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au, can be found in the uncombined free state as the native ore. What does “noble” mean, as used in the term “noble metal”? How is this term related to the occurrence of these metals as the native ore? Why are you unlikely to find a piece of calcium, Ca, when panning for gold, even though Ca is far more abundant on the earth?
36. Heating of carbonates, hydroxides, and certain sulfides converts them to what type of compound?
37. ● (a) What is an alloy? (b) Why are alloys produced? (c) How are alloys produced?
38. ● Describe and illustrate the electrolytic refining of Cu.
39. ● Name the undesirable gaseous product formed during the roasting of copper and other sulfide ores. Why is it undesirable?
40. Bauxite, the principal source of aluminum oxide, contains 55% Al_2O_3 . How much bauxite is required to produce the 5.0×10^6 tons of Al produced annually by electrolysis?
41. ● Write a balanced equation to represent:
(a) the roasting of nickel(II) sulfide to form nickel(II) oxide, and (b) the reduction of nickel(II) oxide by carbon monoxide.

Conceptual Exercises

42. ● One of the problems with roasting sulfide ores is the air pollution caused by the gas that is produced. Describe some consequences of releasing this gas into the atmosphere.
43. ● Gold can be obtained by the separation of gold from the anode sludge of the electrolytic purification of copper. (a) Considering the nature of gold and copper, is this source of gold to be expected? Explain. (b) Would finding silver in the sludge also be expected? Explain.
44. ● The iron formed in a blast furnace is called pig iron, which contains impurities that make the metal brittle. What are these impurities, and how did they come about?
45. ● Discuss how pig iron is refined to form steel.

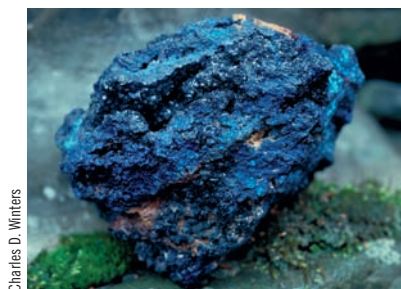
Building Your Knowledge

46. The reaction



takes place in the blast furnace at a temperature of 800. K.

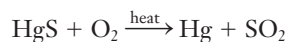
- (a) Calculate ΔH_{800}^0 for this reaction, using $\Delta H_{\text{f},800}^0 = -268 \text{ kJ/mol}$ for FeO, -111 kJ/mol for CO, and -394 kJ/mol for CO_2 . Is this a favorable enthalpy change?
- (b) Calculate ΔG_{800}^0 for this reaction, using $\Delta G_{\text{f},800}^0 = -219 \text{ kJ/mol}$ for FeO, -182 kJ/mol for CO, and -396 kJ/mol for CO_2 . Is this a favorable free energy change?
- (c) Using your values of ΔH_{800}^0 and ΔG_{800}^0 , calculate ΔS_{800}^0 .
47. ● During the operation of a blast furnace, coke reacts with the oxygen in air to produce carbon monoxide, which, in turn, serves as the reducing agent for the iron ore. Assuming the formula of the iron ore to be Fe_2O_3 , calculate the mass of air needed for each ton of iron produced. Assume air to be 21% O_2 by mass, and assume that the process is 91.5% efficient.
48. ● The following reactions take place during the extraction of copper from copper ore.
(a) $2\text{Cu}_2\text{S}(\ell) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{Cu}_2\text{O}(\ell) + 2\text{SO}_2(\text{g})$
(b) $2\text{Cu}_2\text{O}(\ell) + \text{Cu}_2\text{S}(\ell) \longrightarrow 6\text{Cu}(\ell) + \text{SO}_2(\text{g})$
Identify the oxidizing and reducing agents. Show that each equation is correctly balanced by demonstrating that the increase and decrease in oxidation numbers are equal.
49. ▲ Assuming complete recovery of metal, which of the following ores would yield the greater quantity of copper on a mass basis: (a) an ore containing 3.60 mass % azurite, $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$, or (b) an ore containing 4.95 mass % chalcopyrite, CuFeS_2 ?



Charles D. Winters

50. ▲ What mass of copper could be electroplated from a solution of CuSO_4 , using an electric current of 2.50 A flowing for 7.10 h? Assume 100% efficiency.
51. ▲ (a) Calculate the weight, in pounds, of sulfur dioxide produced in the roasting of 1 ton of chalcocite ore containing 10.3% Cu_2S , 0.94% Ag_2S , and no other source of sulfur. (b) What weight of sulfuric acid can be prepared from the SO_2 generated, assuming 83.3% of it can be recovered from stack gases, and 85% of that recovered can be converted to sulfuric acid? (c) How many pounds of pure copper can be obtained, assuming 78% efficient extraction and purification? (d) How many pounds of silver can be produced, assuming 85% of it can be extracted and purified?

52. Which of the following ores of copper has the highest percentage of copper: azurite [$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$], bornite (Cu_5FeS_4), brochantite [$\text{Cu}_4\text{SO}_4(\text{OH})_6$], chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), chalcocite (Cu_2S), cyanotrichite [$\text{Cu}_4\text{Al}_2\text{SO}_4(\text{OH})_{12} \cdot 2\text{H}_2\text{O}$], linarite [$\text{PbCu}(\text{SO}_4)(\text{OH})_2$], and malachite [$\text{Cu}_2\text{CO}_3(\text{OH})_2$]?
53. ▲ Calculate the percentage of iron in hematite ore containing 60.5% Fe_2O_3 by mass. How many pounds of iron would be contained in 1.00 ton of the ore?
54. The roasting of cinnabar, HgS , is a process by which free mercury is obtained.

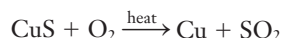


Assuming that the roasting process is 100% efficient, what mass, in tons, of SO_2 is released into the air by the roasting of 376 tons of cinnabar?



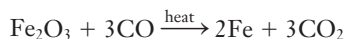
Charles D. Winters

55. The roasting of covellite, CuS , is a process by which free copper is obtained.



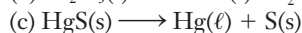
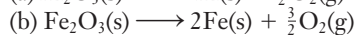
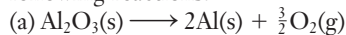
Assuming that the roasting process is 90.5% efficient, what mass, in tons, of SO_2 is released into the air by the roasting of 355 tons of covellite?

56. Consider the separation of iron from hematite, Fe_2O_3 , in a blast furnace that has an overall efficiency of 98.0% in order to leave a specific amount of carbon in the final product.



Calculate the mass of coke, in tons, necessary for the ultimate reaction with 145 tons of hematite.

57. ▲ Using data from Appendix K, calculate ΔG_{298}^0 for the following reactions.



Are any of the reactions spontaneous? Are the ΔG_{298}^0 values in line with what would be predicted based on the relative activities of the metal ions involved? Do increases in temperature favor these reactions?

58. ▲ Find the standard molar enthalpies of formation of Al_2O_3 , Fe_2O_3 , and HgS in Appendix K. Are the values in line with what might be predicted, given the methods by which the metal ions are reduced in extractive metallurgy?

Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

59. Use a reference book or an internet search engine to locate information on the metallurgy of the elements. Answer the following questions. (a) Which of the elements (Cr, Co, or Mo) is not obtained in appreciable amounts during the production of pure copper? (b) Which of the elements (Mn, Cr, or Sb) is not commercially produced by reducing its oxide with aluminum?
60. Use an internet search engine to locate information on the origin of the unit of purity of gold known as the karat (or carat). When was it first used to describe the purity of gold? What is the lowest purity of gold that can be sold as gold in the United States?
61. How many liters of seawater are required to produce a pound of magnesium? Use a seawater density of 1.025 g/cm^3 and assume complete precipitation and/or conversion of the relevant intermediates. (b) How many pounds of oyster shells are needed?
62. Do an internet search to locate information on the chemical composition of iron meteorites. What other element is always present in meteoric alloys? What elements commonly present in manmade steels are absent?



© Ambient Images Inc./Alamy

63. Sterling silver jewelry is frequently stamped “925.” Locate information on the meaning of this number. (a) What does it refer to? (b) What are you getting if you buy a piece of jewelry made from “German silver”?



Metals II: Properties and Reactions

27



Metals and alloys have a wide variety of uses. Strength, lightness, and corrosion resistance are some properties that are required of metals used in aircraft construction.

Louis Psihoyos/Corbis

OUTLINE

The Alkali Metals (Group 1A)

- 27-1** Group 1A Metals: Properties and Occurrence
- 27-2** Reactions of the Group 1A Metals
- 27-3** Uses of Group 1A Metals and Their Compounds

The Alkaline Earth Metals (Group 2A)

- 27-4** Group 2A Metals: Properties and Occurrence
- 27-5** Reactions of the Group 2A Metals
- 27-6** Uses of Group 2A Metals and Their Compounds

The Post-Transition Metals

- 27-7** Group 3A: Periodic Trends

The *d*-Transition Metals

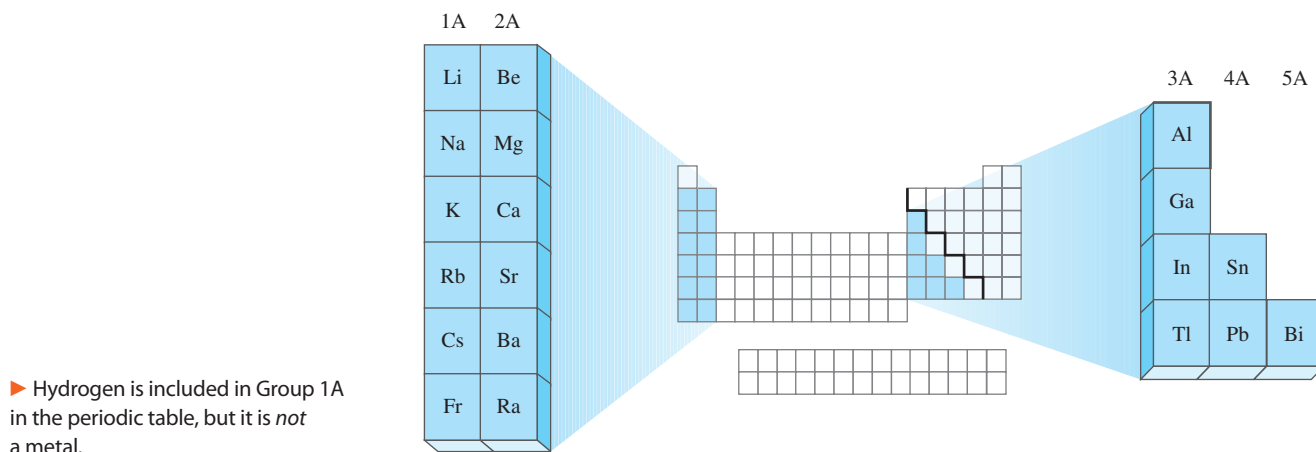
- 27-8** General Properties
- 27-9** Oxidation States
- 27-10** Chromium Oxides, Oxyanions, and Hydroxides

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Describe the properties and occurrence of the Group 1A metals
- ▶ Describe some important reactions of the Group 1A metals
- ▶ Describe some important uses of the Group 1A metals and their compounds
- ▶ Describe the properties and occurrence of the Group 2A metals
- ▶ Describe some important reactions of the Group 2A metals
- ▶ Describe some important uses of the Group 2A metals and their compounds
- ▶ Identify the post-transition metals
- ▶ Describe some important periodic trends in the properties of Group 3A metals and some of their compounds
- ▶ Describe the important properties of aluminum and some of its compounds
- ▶ Identify the *d*-transition metals and describe some of their important properties and their typical compounds
- ▶ Describe typical oxidation states of the transition metals
- ▶ Describe some oxides, oxyanions, and hydroxides of chromium

In this chapter we will discuss some **representative metals** and some ***d*-transition metals**. The representative elements are those in the A groups of the periodic table. They have valence electrons in their outermost *s* or *p* atomic orbitals. Metallic character increases from top to bottom within groups and from right to left within periods. All the elements in Groups 1A (except H) and 2A are metals. The heavier members of Groups 3A, 4A, and 5A are called **post-transition metals**.



The Alkali Metals (Group 1A)

27-1 Group 1A Metals: Properties and Occurrence

- ▶ See the discussion of electrolysis of sodium chloride in Section 21-3.

The alkali metals are not found free in nature because they are so easily oxidized. They are most economically produced by electrolysis of their molten salts. Sodium (2.6% abundance by mass) and potassium (2.4% abundance) are very common in the earth's crust. The other 1A metals are quite rare. Francium consists only of short-lived radioactive isotopes formed by alpha-particle emission from actinium (see Section 22-4). Both potassium and cesium also have natural radioisotopes. Potassium-40 is important in the potassium-argon radioactive decay method of dating ancient objects (see Section 22-12). The properties of the alkali metals vary regularly as the group is descended (Table 27-1).

Table 27-1 Properties of the Group 1A Metals

Property	Li	Na	K	Rb	Cs	Fr
Outer electrons	2s ¹	3s ¹	4s ¹	5s ¹	6s ¹	7s ¹
Melting point (°C)	186	97.8	63.6	38.9	28.5	27
Boiling point (°C)	1347	904	774	688	678	677
Density (g/cm ³)	0.534	0.971	0.862	1.53	1.87	—
Atomic radius (Å)	1.52	1.86	2.27	2.48	2.65	—
Ionic radius, M ⁺ (Å)	0.90	1.16	1.52	1.66	1.81	—
Electronegativity	1.0	1.0	0.9	0.9	0.8	0.8
E^0 (volts): M ⁺ (aq) + e [−] → M(s)	−3.05	−2.71	−2.93	−2.93	−2.92	—
Ionization energies (kJ/mol)						
M(g) → M ⁺ (g) + e [−]	520	496	419	403	377	—
M ⁺ (g) → M ²⁺ (g) + e [−]	7298	4562	3051	2632	2420	—
$\Delta H^0_{\text{hydration}}$ (kJ/mol): M ⁺ (g) + xH ₂ O → M ⁺ (aq)	−544	−435	−351	−293	−264	—

The free Group 1A metals, except lithium, are soft, silvery, highly reactive metals that can be cut with a knife; lithium is harder. Cesium is slightly golden and melts at 28.5°C (just below body temperature). The relatively low melting and boiling points of the alkali metals result from their fairly weak bonding forces. Each atom can furnish only one electron for metallic bonding (see Section 13-17). Because their outer electrons are so loosely held, the metals are excellent electrical and thermal conductors. They ionize when irradiated with low-energy light (the photoelectric effect). These effects become more pronounced with increasing atomic size. Cesium is used in photoelectric cells.

The low ionization energies of the 1A metals show that the single electron in the outer shell is very easily removed. In all alkali metal compounds, the metals exhibit the +1 oxidation state. Virtually all such compounds are ionic. The extremely high second ionization energies show that removal of an electron from a filled shell is impossible by chemical means.

We might expect the standard reduction potentials of the metal ions to become less favorable (more negative) as the ionization energies for the metal atoms become more favorable (less endothermic). The magnitude of the standard reduction potential of Li, −3.05 volts, is unexpectedly large, however. The first ionization energy is the amount of energy absorbed when a mole of *gaseous* atoms ionize. The standard reduction potential, E^0 , indicates the ease with which *aqueous* ions are reduced to the metal (see Section 21-14). Thus, hydration energies must also be considered (see Section 14-2). Because the Li⁺ ion is so small, its charge density (ratio of charge to size) is very high. It therefore exerts a stronger attraction for polar H₂O molecules than do the other 1A ions. These H₂O molecules must be stripped off during the reduction process in a very endothermic manner, making the E^0 for the Li⁺/Li couple very negative (see Table 27-1).

The high charge density of Li⁺ ion accounts for its ability to polarize large anions. This gives a higher degree of covalent character in Li compounds than in other corresponding alkali metal compounds. For example, LiCl is soluble in ethyl alcohol, a less polar solvent than water; NaCl is not. Salts of the alkali metals with small anions are very soluble in water, but salts with large and complex anions, such as silicates and aluminosilicates, are not very soluble.



Charles D. Winters

Sodium, like the other alkali metals, is an excellent conductor of electricity.

► **Polarization** of an anion refers to distortion of its electron cloud. The ability of a cation to polarize an anion increases with increasing charge density (ratio of charge to size) of the cation.

27-2 Reactions of the Group 1A Metals

Many of the reactions of the alkali metals are summarized in Table 27-2. All are characterized by the loss of one electron per metal atom. These metals are very strong reducing agents. Reactions of the alkali metals with H₂ and O₂ were discussed in Sections 5-8 and 5-9, reactions with the halogens in Section 7-2, and reactions with water in Section 6-10, Part 2.

Unless otherwise noted, all content on this page is © Cengage Learning.

Trace Elements and Life

More than 300 years ago, iron was the first trace element shown to be essential in the human diet. An English physician, Thomas Sedenham, soaked “iron and steel filings” in cold Rhenish wine. He used the resulting solution to treat patients suffering from chlorosis, now known to be an iron deficiency anemia. Nearly 20 trace elements are now believed to be required by humans. The discovery of the biological functions of trace elements is an exciting and controversial area of human nutrition research.

The trace elements can be classified into several categories (see tables on next page). In 1989, the National Research Council recognized that iron, iodine, zinc, selenium, copper, chromium, manganese, and molybdenum were dietary essentials for humans. Fluorine is also considered to be valuable for human health because of its benefits to the teeth and skeleton. These nine trace elements are required by humans and other animals because they are essential components in metalloenzymes and hormones or because they promote health in a specific tissue (such as fluorine in the teeth and skeleton). The trace elements required by the human body in milligram quantities include iron, zinc, copper, manganese, and fluorine. Trace elements required in microgram (μg) quantities include iodine, selenium, chromium, and molybdenum. Although probably required in μg quantities, no dietary recommendations have been made for arsenic, nickel, silicon, and boron even though there is evidence, primarily from animals, that they are essential. There is only weak evidence that cadmium, lead, lithium, tin, vanadium, and bromine are essential for humans.

Iron deficiency is one of the most common nutrient deficiencies in the world, occurring in up to 60% of the women, infants, and children of some countries. Anemia, characterized by a low concentration of hemoglobin in the blood or by a low volume of packed red blood cells, is the usual symptom of iron deficiency. Other symptoms include fatigue and cognitive disorders. Up to 1% of the population may have the genetic disease known as hereditary hemochromatosis, which results in excess absorption of dietary iron and can lead to liver and heart damage. Con-

cern about this disease may eventually lead to routine screening so that persons with this disorder can be treated before severe symptoms develop and can avoid foods and supplements with large amounts of iron. The recommended dietary allowance for iron for women aged 23 to 50 years is 50% higher than that for men in the same age group because of the iron lost in menstrual bleeding.

Iodine deficiency remains a major cause of mental retardation and infant mortality and morbidity worldwide—even though iodine was shown to be essential for human health nearly 100 years ago. More than 1 billion people are believed to be at risk for iodine deficiency. In 1986, the International Council for the Control of Iodine Deficiency Disorders was established in an effort to improve iodine nutrition and alleviate human suffering. This council works closely with the World Health Organization, the United Nations International Children’s Fund, and the United Nations to alleviate iodine deficiency. Iodine is required for the thyroid hormones, thyroxine and triiodothyronine, that regulate the metabolic rate and O_2 consumption of cells. Iodine is also intimately involved in the control of growth and development, particularly during fetal and infant life.

In the 1930s, zinc was discovered to be a dietary essential in animals. Zinc deficiency was recognized as a potential public health problem in the 1960s in Iran, where endemic hypogonadism (delayed sexual development) and dwarfism were discovered in adolescents consuming insufficient dietary zinc. More than 200 zinc enzymes have been discovered. Zinc is also important for the structure and function of biomembranes. Loss of zinc from these membranes results in increased susceptibility to oxidative damage, structural strains, and alterations in specific receptor sites and transport systems. Zinc also helps to stabilize the structures of RNA, DNA, and ribosomes. Several transcription factors contain “Zn fingers,” which are needed for the binding of these transcription factors to the DNA. Thus, zinc is absolutely necessary for adequate growth, protein synthesis, and cell division. The best sources of zinc in the human diet are animal foods such as meat, fish, poultry, and dairy products.



Many dietary supplements include essential trace elements.

Dietary Trace Elements

Known to Be Essential	Known or Suspected Functions
iron	Hemoglobin, energy metabolism
iodine	Thyroid hormones
zinc	Enzymes, protein synthesis, cell division
copper	Hemoglobin, bone, nerves, vascular system
selenium	Enzymes, protect against oxidant stress
chromium	Insulin action
manganese	Enzymes, bone
molybdenum	Enzymes, sulfur metabolism
fluorine	Bones, teeth
Substantial Evidence for Essentiality	Known or Suspected Functions
arsenic	Amino acid metabolism
boron	Metabolism of calcium, magnesium, hormones
nickel	Not known, suspected in some enzymes
silicon	Bone and connective tissue
Weak Evidence for Essentiality	Known or Suspected Functions
bromine	Not yet known
cadmium	Not yet known
lead	Not yet known
lithium	Not yet known
tin	Not yet known
vanadium	Not yet known

Copper was also shown to be essential in the early 1900s. Copper is needed for the absorption and mobilization of iron, so a deficiency of copper causes a type of anemia that is difficult to distinguish from iron deficiency anemia. Copper is also needed for the cardiovascular system, bone, brain, and nervous system. Premature and malnourished infants are particularly susceptible to developing copper deficiency, in part because milk is a poor source of copper. Whole grains, legumes, and nuts are the major dietary sources of copper.

Selenium was first suspected of being a dietary essential in the 1950s. Selenium is considered to be an antioxidant nutrient because it is present in enzymes that help protect against toxic species of oxygen and free radicals. Selenium deficiency is a major public health problem in certain parts of China, where it increases the risk of heart disease, bone and joint disorders, and liver cancer. Selenium is currently under intensive investigation as a possible protector against cancer. The content of selenium in foods is highly variable and dependent on the selenium content of the soil. Generally the best sources of selenium are muscle meats, cereals, and grains.

The 1950s also saw the first evidence that chromium might be a dietary essential. Chromium is believed to promote the action of insulin and thus influences the metabolism of carbohydrates, fats, and proteins. Reports of severe human deficiency of chromium are rare and have been found primarily in people receiving only intravenous feedings for several months or years. Only a few laboratories in the world can accurately measure the amount of chromium in foods and body tissues because chromium is present in stainless steel, which is ubiquitous in analytical laboratories and easily contaminates biological samples.

Manganese and molybdenum are essential for enzymes in humans and other animals, but a dietary deficiency of these minerals is exceedingly rare in humans. Cobalt is essential for vitamin B₁₂, but the human body cannot make vitamin B₁₂ from cobalt and thus requires the preformed vitamin from dietary sources. (It is possible to derive some vitamin B₁₂ from bacterial synthesis in the digestive tract.)

Efforts to discover whether other elements might be essential intensified during the 1970s. Although it is believed that arsenic, nickel, silicon, and boron are probably essential to humans, it has been difficult to determine whether other minerals have specific biological functions in humans or other animals.

There are several reasons why it is difficult to establish the essentiality of trace elements. Some elements, such as arsenic and selenium, were first recognized for their extreme toxicity, so it has been difficult to convince many health specialists that a toxic element might also be a dietary essential at low levels. Also, most trace elements are present in extremely small amounts in diets and in tissues, and few laboratories are equipped to prevent contamination of samples and to measure these elements with the necessary precision.

Two factors have aided in the discovery of the roles of many trace elements. One is the availability of two highly sensitive analytical techniques, activation analysis and electrothermal atomic absorption spectroscopy, that allow detection of these elements in concentrations of only a few parts per billion. The other is the use of special isolation chambers that allow study of animals under carefully controlled conditions, free of unwanted contaminants. Animals' diets and their air supply must be carefully purified to keep out even traces of unwanted elements, and their cages must be made of plastics that contain no metals.

Our understanding of the biological functions of trace elements is changing the way scientists think about diet and health. For example, supplements of manganese, copper, and zinc in combination with calcium have recently been shown to improve human bone health to a greater extent than just calcium alone. Silicon and boron are also believed to be important for bone health. Deficiencies of selenium or copper are suspected by some scientists of increasing the risk of cancer or heart disease. Because chromium, copper, and zinc influence glucose metabolism, future prevention and treatment strategies for diabetes may involve these nutrients.

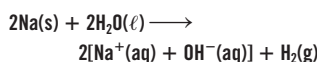
MARY ANN JOHNSON
COLLEGE OF FAMILY AND CONSUMER SCIENCES
UNIVERSITY OF GEORGIA

Unless otherwise noted, all content on this page is © Cengage Learning.



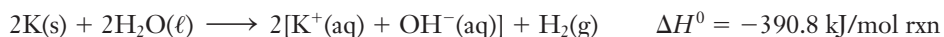
Charles Steele

Sodium reacts vigorously with water.



The indicator phenolphthalein was added to the water. As NaOH forms, the solution turns pink.

The high reactivities of the alkali metals are illustrated by their vigorous exothermic reactions with water. Lithium reacts readily; sodium reacts so vigorously that the hydrogen gas it forms may ignite; and potassium, rubidium, and cesium cause the H_2 to burst into flames when the metals are dropped into water. The large amounts of heat evolved provide the activation energy to ignite the hydrogen. The elements also react with water vapor in the air or with moisture from the skin.



Alkali metals are stored under anhydrous nonpolar liquids such as mineral oil.

As is often true for elements of the second period, Li differs in many ways from the other members of its family. Its ionic charge density and electronegativity are close to those of Mg, so Li compounds resemble those of Mg in some ways. This illustrates the **diagonal similarities** that exist between elements in successive groups near the top of the periodic table.

1A	2A	3A	4A
Li	Be	B	C
Na	Mg	Al	Si

Lithium is the only 1A metal that combines with N_2 to form a nitride, Li_3N . Magnesium readily forms magnesium nitride, Mg_3N_2 . Both metals readily combine with carbon to form carbides, whereas the other alkali metals do not react readily with carbon. The solubilities of Li compounds are closer to those of Mg compounds than to those of other 1A compounds. The fluorides, phosphates, and carbonates of both Li and Mg are only slightly soluble, but their chlorides, bromides, and iodides are very soluble. Both Li and Mg form normal oxides, Li_2O and MgO , when burned in air at 1 atmosphere pressure. The other alkali metals typically form peroxides or superoxides.

The 1A metal oxides are basic anhydrides (see Section 5-9). They react with water to form strong bases.

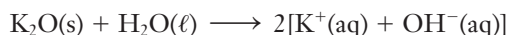
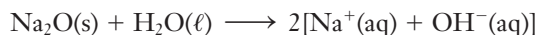


Table 27-2 Some Reactions of the Group 1A Metals

Reaction	Remarks
$4\text{M} + \text{O}_2 \longrightarrow 2\text{M}_2\text{O}$	Limited O_2
$4\text{Li} + \text{O}_2 \longrightarrow 2\text{Li}_2\text{O}$	Excess O_2 (lithium oxide)
$2\text{Na} + \text{O}_2 \longrightarrow \text{Na}_2\text{O}_2$	(sodium peroxide)
$\text{M} + \text{O}_2 \longrightarrow \text{MO}_2$	$\text{M} = \text{K, Rb, Cs}$; excess O_2 (superoxides)
$2\text{M} + \text{H}_2 \longrightarrow 2\text{MH}$	Molten metals
$6\text{Li} + \text{N}_2 \longrightarrow 2\text{Li}_3\text{N}$	Reacts slowly at room temperature
$2\text{M} + \text{X}_2 \longrightarrow 2\text{MX}$	$\text{X} = \text{halogen (Group 7A)}$
$2\text{M} + \text{S} \longrightarrow \text{M}_2\text{S}$	Also with Se, Te of Group 6A
$12\text{M} + \text{P}_4 \longrightarrow 4\text{M}_3\text{P}$	
$2\text{M} + 2\text{H}_2\text{O} \longrightarrow 2\text{MOH} + \text{H}_2$	K, Rb, and Cs react explosively
$2\text{M} + 2\text{NH}_3 \longrightarrow 2\text{MNH}_2 + \text{H}_2$	With $\text{NH}_3(\text{l})$ in presence of catalyst; with $\text{NH}_3(\text{g})$ at high temperature (solutions also contain $\text{M}^+ + \text{solvated } e^-$)

27-3 Uses of Group 1A Metals and Their Compounds

Lithium, Li

Metallic lithium has the highest heat capacity of any element. It is used as a heat transfer medium in experimental nuclear reactors. Extremely lightweight lithium–aluminum alloys are used in aircraft construction. Lithium compounds are used in some lightweight dry cells and storage batteries because they have very long lives, even in extreme temperatures. LiCl and LiBr are very hygroscopic (they take up moisture readily) and are used in industrial drying processes and air conditioning. Lithium compounds are used for the treatment of some types of mental disorders, mainly manic depression.

► The highly corrosive nature of both lithium and sodium is a major drawback for applications of the pure metals.

Sodium, Na

Sodium is by far the most widely used alkali metal because it is so abundant. Its salts are essential for life. The metal itself is used as a reducing agent in the manufacture of drugs and dyes and in the metallurgy of such metals as titanium and zirconium.



Highway lamps often incorporate Na arcs, which produce a bright yellow glow. A few examples of the uses of sodium compounds are NaOH, called caustic soda, lye, or soda lye (used for production of rayon, cleansers, textiles, soap, paper, and many polymers); Na_2CO_3 , called soda or soda ash, and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, called washing soda (also used as a substitute for NaOH when a weaker base is acceptable); NaHCO_3 , called baking soda or bicarbonate of soda (used for baking and other household uses); NaCl (used as table salt and as the source of all other compounds of Na and Cl); NaNO_3 , called Chile saltpeter (a nitrogen fertilizer); Na_2SO_4 , called salt cake, a by-product of HCl manufacture (used for production of brown wrapping paper and cardboard boxes); and NaH (used for synthesis of NaBH_4 , which is used to recover silver and mercury from wastewater).



The yellowish glow of some highway lamps is due to a sodium arc. Mercury lamps give a bluish-green glow.



Lithium



Sodium



Potassium

Spacings of energy levels are different for different alkali metals. The salts of the alkali metals impart characteristic colors to flames: lithium (*red*), sodium (*yellow*), and potassium (*violet*).

Unless otherwise noted, all content on this page is © Cengage Learning.

Other Group 1A Metals

Like salts of Na, those of potassium are essential for life. KNO_3 , commonly known as niter or saltpeter, is used as a potassium and nitrogen fertilizer. Most other major industrial uses for K can be satisfied with the more abundant and less expensive Na.

There are very few practical uses for the rare metals rubidium, cesium, and francium. Cesium is used in some photoelectric cells (see Section 4-12).

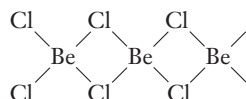
The Alkaline Earth Metals (Group 2A)

27-4 Group 2A Metals: Properties and Occurrence

The alkaline earth metals are all silvery white, malleable, ductile, and somewhat harder than their neighbors in Group 1A. Activity increases from top to bottom within the group, with Ca, Sr, and Ba being considered quite active. Each has two electrons in its highest occupied energy level. Both electrons are lost in ionic compound formation, though not as easily as the outer electron of an alkali metal. Compare the ionization energies in Tables 27-1 and 27-3. Most 2A compounds are ionic, but those of Be exhibit a great deal of covalent character. This is due to the extremely high charge density of Be^{2+} . Compounds of beryllium therefore resemble those of aluminum in Group 3A (diagonal similarities). The 2A elements exhibit the +2 oxidation state in all their compounds. The tendency to form 2+ ions increases from Be to Ra.

The alkaline earth metals show a wider range of chemical properties than the alkali metals. The 2A metals are not as reactive as the 1A metals, but they are much too reactive to occur naturally in their elemental states. They are obtained by electrolysis of their molten chlorides. Calcium and magnesium are abundant in the earth's crust, especially as carbonates and sulfates. Beryllium, strontium, and barium are less abundant. All known radium isotopes are radioactive and are extremely rare.

► In Section 8-5 we found that gaseous BeCl_2 is linear. The Be atoms in BeCl_2 molecules, however, act as Lewis acids. In the solid state, the Cl atoms form coordinate covalent bonds to Be, resulting in a polymeric structure. In such compounds, Be follows the octet rule.



► Amphoterism is the ability of a substance to react with both acids and bases (see Section 10-6).

27-5 Reactions of the Group 2A Metals

Table 27-4 summarizes some reactions of the alkaline earth metals, which, except for stoichiometry, are similar to the corresponding reactions of the alkali metals. Reactions with hydrogen and oxygen were discussed in Sections 5-8 and 5-9.

Except for Be, all the alkaline earth metals are oxidized to oxides in air. The 2A oxides (except BeO) are basic and react with water to give hydroxides. Beryllium hydroxide,

Table 27-3 Properties of the Group 2A Metals

Property	Be	Mg	Ca	Sr	Ba	Ra
Outer electrons	$2s^2$	$3s^2$	$4s^2$	$5s^2$	$6s^2$	$7s^2$
Melting point ($^{\circ}\text{C}$)	1283	649	839	770	725	700
Boiling point ($^{\circ}\text{C}$)	2484	1105	1484	1384	1870	1737
Density (g/cm^3)	1.85	1.74	1.55	2.60	3.51	5
Atomic radius ($\text{\AA}$)	1.12	1.60	1.97	2.15	2.22	2.20
Ionic radius, M^{2+} ($\text{\AA}$)	0.59	0.85	1.14	1.32	1.49	—
Electronegativity	1.5	1.2	1.0	1.0	1.0	1.0
E^0 (volts): $\text{M}^{2+}(\text{aq}) + 2e^- \longrightarrow 2\text{M}(\text{s})$	-1.85	-2.37	-2.87	-2.89	-2.90	-2.92
Ionization energies (kJ/mol)						
$\text{M}(\text{g}) \longrightarrow \text{M}^+(\text{g}) + e^-$	899	738	599	550	503	509
$\text{M}^+(\text{g}) \longrightarrow \text{M}^{2+}(\text{g}) + e^-$	1757	1451	1145	1064	965	(979)
$\Delta H_{\text{hydration}}^0$ (kJ/mol): $\text{M}^{2+}(\text{g}) \longrightarrow \text{M}^{2+}(\text{aq})$	—	-1925	-1650	-1485	-1276	—

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 27-4 Some Reactions of the Group 2A Metals

Reaction	Remarks
$2M + O_2 \longrightarrow 2MO$	Very exothermic (except Be)
$Ba + O_2 \longrightarrow BaO_2$	Almost exclusively
$M + H_2 \longrightarrow MH_2$	M = Ca, Sr, Ba at high temperatures
$3M + N_2 \longrightarrow M_3N_2$	At high temperatures
$6M + P_4 \longrightarrow 2M_3P_2$	At high temperatures
$M + X_2 \longrightarrow MX_2$	X = halogen (Group 7A)
$M + S \longrightarrow MS$	Also with Se, Te of Group 6A
$M + 2H_2O \longrightarrow M(OH)_2 + H_2$	M = Ca, Sr, Ba at 25°C; Mg gives MgO at high temperatures
$M + 2NH_3 \longrightarrow M(NH_2)_2 + H_2$	M = Ca, Sr, Ba in $NH_3(l)$ in presence of catalyst; $NH_3(g)$ with heat

$Be(OH)_2$, is quite insoluble in water and is amphoteric. Magnesium hydroxide, $Mg(OH)_2$, is only slightly soluble in water. The hydroxides of Ca, Sr, and Ba are strong bases.

Beryllium is at the top of Group 2A. Its oxide is amphoteric, whereas oxides of the heavier members are basic anhydrides (see Section 5-9). Metallic character increases from top to bottom within a group and from right to left across a period. This results in increasing basicity and decreasing acidity of the oxides in the same directions, as shown in the following table.

	Group 1A	Group 2A	Group 3A
	Li_2O (basic)	BeO (amphoteric)	B_2O_3 (amphoteric)
	Na_2O (basic)	MgO (basic)	Al_2O_3 (amphoteric)
	K_2O (basic)	CaO (basic)	Ga_2O_3 (amphoteric)
			In_2O_3 (basic)

Beryllium does not react with pure water even at red heat. It reacts with solutions of strong bases to form the complex ion, $[Be(OH)_4]^{2-}$, and H_2 . Magnesium reacts with steam to produce MgO and H_2 . Ca, Sr, and Ba react with water at 25°C to form hydroxides and H_2 (see Table 27-4). Group 2A compounds are generally less soluble in water than corresponding 1A compounds, but many are quite soluble.

27-6 Uses of Group 2A Metals and Their Compounds

Beryllium, Be

Because of its rarity, beryllium has only a few practical uses. It occurs mainly as beryl, $Be_3Al_2Si_6O_{18}$, a gemstone which, with appropriate impurities, may be aquamarine (blue) or emerald (green). Because it is transparent to X-rays, “windows” for X-ray tubes are constructed of beryllium. Beryllium compounds are quite toxic.



Charles D. Winters

Magnesium burns in air.



© Photodisc Green/Getty

Calcium carbonate and calcium phosphate occur in seashells and animal bones.



Charles Steele



A laboratory X-ray tube (left) and a close-up view of one of its windows (right). The windows are made of beryllium metal.

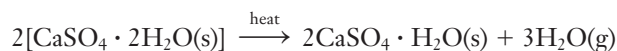
Magnesium, Mg

Metallic magnesium burns in air with such a brilliant white light that it is used in flares and fireworks. It is very lightweight and is currently used in many alloys for building materials. Like aluminum, it forms an impervious coating of oxide that protects it from further oxidation. Given its inexhaustible supply in the oceans, it is likely that many more structural uses will be found for it as the reserves of iron ores dwindle.

Calcium, Ca

Calcium and its compounds are widely used commercially. The element is used as a reducing agent in the metallurgy of uranium, thorium, and other metals. It is also used as a scavenger to remove dissolved impurities such as oxygen, sulfur, and carbon in molten metals and to remove residual gases in vacuum tubes. It is a component of many alloys.

Heating limestone, CaCO_3 , produces *quicklime*, CaO , which can then be treated with water to form *slaked lime*, Ca(OH)_2 , an inexpensive base for which industry finds many uses. When slaked lime is mixed with sand and exposed to the CO_2 of the air, it hardens to form mortar. Heating gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, produces plaster of Paris, $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$.



Strontium, Sr

Strontium salts are used in fireworks and flares, which show the characteristic red glow of strontium in a flame. Strontium chloride is used in some toothpastes for persons with sensitive teeth. The metal itself has no practical uses.

Barium, Ba

Barium is a constituent of alloys that are used for spark plugs because of the ease with which it emits electrons when heated. It is used as a degassing agent for vacuum tubes. A slurry of finely divided barium sulfate, BaSO_4 , is used to coat the gastrointestinal tract in preparation for X-ray photographs because it absorbs X-rays so well. All soluble barium salts are very toxic, but BaSO_4 is so insoluble that it is not poisonous.

The Post-Transition Metals

The metals below the stepwise division of the periodic table in Groups 3A through 5A are the **post-transition metals**. These include aluminum, gallium, indium, and thallium from Group 3A; tin and lead from Group 4A; and bismuth from Group 5A. Aluminum is the only post-transition metal that is considered very reactive. We will focus our discussion on the metals of Group 3A.

► There are no true metals in Groups 6A, 7A, or 8A.

27-7 Group 3A: Periodic Trends

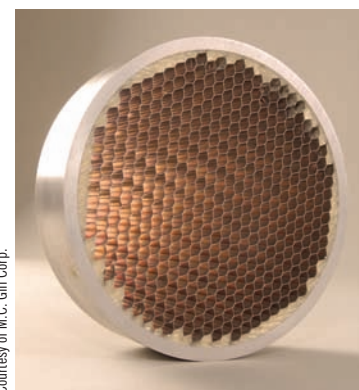
The properties of the elements in Group 3A (Table 27-5) vary less regularly down the groups than those of the 1A and 2A metals. The Group 3A elements are all solids. Boron, at the top of the group, is a nonmetal. Its melting point, 2300°C, is very high because it crystallizes as a covalent solid. The other elements, aluminum through thallium, form metallic crystals and have considerably lower melting points.

Aluminum, Al

Aluminum is the most reactive of the post-transition metals. It is the most abundant metal in the earth's crust (7.5%) and the third most abundant element. Aluminum is inexpensive compared with most other metals. It is soft and can be readily extruded into wires or rolled, pressed, or cast into shapes.

Because of its relatively low density, aluminum is often used as a lightweight structural metal. It is often alloyed with Mg and some Cu and Si to increase its strength. Many buildings are sheathed in aluminum, which resists corrosion by forming a tough and stable oxide coating.

Pure aluminum conducts about two-thirds as much electric current per unit volume as copper, but it is only one-third as dense (Al, 2.70 g/cm³; Cu, 8.92 g/cm³). As a result, a given mass of aluminum can conduct twice as much current as the same mass of copper. Aluminum is now used in electrical transmission lines and has been used in wiring in homes. The latter use has been implicated as a fire hazard, however, due to the heat that



Courtesy of M.C. Gill Corp.

This aluminum honeycomb material is made by bonding aluminum foil sheets to form hexagonal cells. It is used to make sandwich construction panels that have a very high strength-to-weight ratio.

Table 27-5 Properties of the Group 3A Elements

Property	B	Al	Ga	In	Tl
Outer electrons	$2s^22p^1$	$3s^23p^1$	$4s^24p^1$	$5s^25p^1$	$6s^26p^1$
Physical state (25°C, 1 atm)	solid	solid	solid	solid	solid
Melting point (°C)	2300	660	29.8	156.6	303.5
Boiling point (°C)	2550	2367	2403	2080	1457
Density (g/cm ³)	2.34	2.70	5.91	7.31	11.85
Atomic radius (Å)	0.85	1.43	1.35	1.67	1.70
Ionic radius, M ³⁺ (Å)	(0.20)*	0.68	0.76	0.94	1.03
Electronegativity	2.0	1.5	1.7	1.6	1.6
E^0 (volts): $M^{3+}(aq) + 3e^- \longrightarrow M(s)$	(-0.90)*	-1.66	-0.53	-0.34	0.916
Oxidation states	-3 to +3	+3	+1, +3	+1, +3	+1, +3
Ionization energies (kJ/mol)					
$M(g) \longrightarrow M^+(g) + e^-$	801	578	579	558	589
$M^+(g) \longrightarrow M^{2+}(g) + e^-$	2427	1817	1971	1813	1961
$M^{2+}(g) \longrightarrow M^{3+}(g) + e^-$	3660	2745	2952	2692	2867
$\Delta H_{\text{hydration}}^0$ (kJ/mol): $M^{3+}(g) + xH_2O \longrightarrow M^{3+}(aq)$	—	-4750	-4703	-4159	-4117

*For the covalent +3 oxidation state.

Unless otherwise noted, all content on this page is © Cengage Learning.

can be generated during high current flow at the junction of the aluminum wire and fixtures of other metals. As a result, aluminum wiring no longer meets building codes in many places.

Aluminum is a strong reducing agent.



Aluminum is thus quite reactive, but a thin, very hard transparent film of Al_2O_3 forms when Al comes into contact with air. This protects it from further oxidation. The oxide coating, however, does not usually protect it from most acids. $\text{H}^{+}(\text{aq})$ can penetrate microcracks in the oxide layer and react with the aluminum metal underneath. Oxidizing acids such as nitric acid, HNO_3 , however, oxidize the aluminum metal to Al_2O_3 , which protects the underlying metal.

The very negative enthalpy of formation of aluminum oxide makes Al a very strong reducing agent for other metal oxides. The *thermite reaction* is a spectacular example. It generates enough heat to produce molten iron for welding large steel parts such as shafts and train tracks (Figure 27-1).



Anhydrous Al_2O_3 occurs naturally as the extremely hard, high-melting mineral *corundum*, which has a network structure. It is colorless when pure, but becomes colored when transition metal ions replace a few Al^{3+} ions in the crystal. *Sapphire* is usually blue and contains some iron and titanium. *Ruby* is red due to the presence of small amounts of chromium.

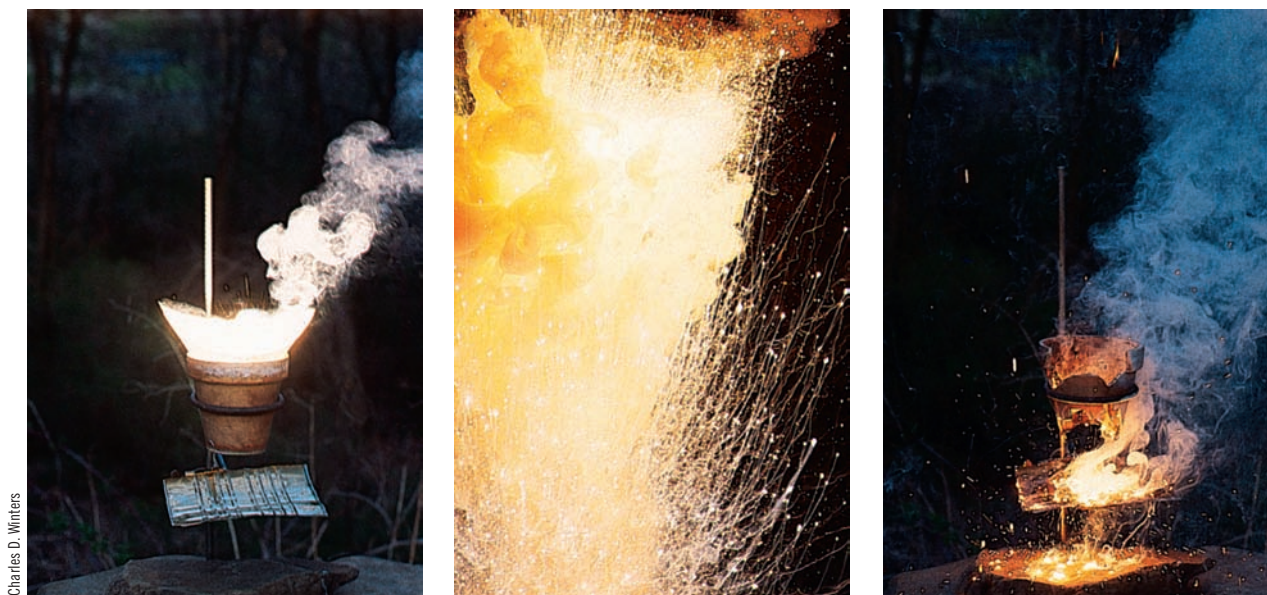


© Geological Institute of America

Small amounts of different transition metal ions give different colors to sapphire, which is mostly aluminum oxide, Al_2O_3 .

Other Group 3A Metals

Gallium is an unusual metal in that it melts when held in the hand. It has the largest liquid state temperature range of any element (29.8° to 2403°C). It is used in transistors and high-temperature thermometers. Gallium-67 was one of the first artificially produced isotopes to be used in medicine. It concentrates in inflamed areas and in certain melanomas.



Charles D. Winters

A The reaction was initiated by lighting the magnesium fuse.

B So much heat was produced by the reaction that the iron melted as it was produced.

C The molten iron dropped out of the clay pot and burned through a sheet of iron that was placed under the pot.

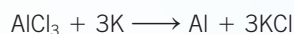
Figure 27-1 The thermite reaction. A mixture of Fe_2O_3 and aluminum powder was placed in a clay pot with a piece of magnesium ribbon as a fuse.

CHEMISTRY IN USE

The Most Valuable Metal in the World

Imagine paying \$8 million for one pound of aluminum! Although aluminum currently costs less than \$1.00 a pound, it was considered the most valuable metal in 1827. Aluminum was so cherished by royalty in the early to mid-1800s that they alone ate with aluminum spoons and forks, while their lower-class guests dined with cheaper gold and silver service. Aluminum is the most abundant metal in the earth's crust (7.5%); why was it originally so expensive?

Aluminum was first prepared by the following displacement reaction.



Potassium was also expensive because it was made by passing an electric current (from a voltaic cell) through molten KCl. In addition to the great cost of energy required to melt large quantities of KCl, copper and zinc (used in voltaic cells) were also expensive metals in the early 1800s. Thus, the very small amount of aluminum produced by this displacement reaction was extremely expensive.

It was not practical to produce aluminum by passing an electric current through molten Al_2O_3 because it has a high melting point, 2000°C. This high temperature is difficult to achieve and maintain; the components of most voltaic cells melt below this temperature. Zinc melts at 420°C and copper at 1083°C.

The cost of aluminum began to drop as the result of two major advances in the late 1800s. The first came with the invention of the electric generator, which could produce electricity using steam or water. Electricity generated by steam or water was quite inexpensive compared with electricity generated by voltaic cells. Despite this cost reduction, aluminum still cost

more than \$100,000 a pound. The second advance took place in 1886, when chemists discovered that they could lower the melting point of aluminum oxide by mixing it with complex salts, such as $\text{Na}_3[\text{AlF}_6]$. Since 1886, the price of aluminum has decreased markedly because of lower electricity costs, improved production techniques, and recycling of discarded aluminum products.

Although aluminum is no longer used in table services by royalty, it is of inestimable value in energy conservation. Around our homes we find energy-saving items such as aluminum storm doors and windows, insulation backed with aluminum foil, and aluminum siding. Because vehicle weight significantly affects gas mileage, substituting aluminum for heavier metals in cars, trucks, trains, and aircraft helps preserve our petroleum supplies. Although the cost of aluminum has decreased drastically, it is still a valuable metal because of its ability to help us conserve energy and to improve our standard of living at the same time.

RONALD DELORENZO



Charles D. Winters

Indium is a soft, bluish metal that is used in some alloys with silver and lead to make good heat conductors. Most indium is used in electronics. Thallium is a soft, heavy metal that resembles lead. It is quite toxic and has no important practical uses as a free metal.

Periodic Trends

The atomic radii do not increase regularly as Group 3A is descended (see Figure 5-1). The atomic radius of Ga, 1.35 Å, is *less* than that of Al, 1.43 Å, which is directly above Ga. The transition elements are located between calcium (2A) and gallium (3A), strontium (2A) and indium (3A), and barium (2A) and thallium (3A). The increase in nuclear charge that accompanies filling of the $(n - 1)d$ subshell results in the contraction of the size of the atoms. This contraction is caused by the stronger attraction of the more highly charged nuclei for the outer electrons. This causes the radii of Ga, In, and Tl to be smaller than would be predicted from the radii of B and Al. Atomic radii strongly influence other properties. For example, Ga, In, and Tl are each much denser than the elements above them due to their unusually small atomic radii.

The Group 3A elements have the ns^2np^1 outer electron configuration. Aluminum shows only the +3 oxidation state in its compounds. The heavier metals (Ga, In, Tl) can lose or



Gallium metal melts below body temperature.

► Compare the radii and densities of these elements with those of Group 1A and 2A metals in the same rows.

Unless otherwise noted, all content on this page is © Cengage Learning.

► As is generally true, for each pair of compounds, covalent character is greater for the higher (more polarizing) oxidation state of the metal.

share either the single p valence electron or the p and both s electrons to exhibit the +1 or +3 oxidation state, respectively. In general the post-transition metals can exhibit oxidation states of $(g - 2)+$ and $g+$, where g = periodic group number. As examples, $TiCl$ and $TiCl_3$ both exist, as do $SnCl_2$ and $SnCl_4$. The stability of the lower state increases as the groups are descended. This is called the **inert s -pair effect** because the two s electrons remain nonionized, or unshared, for the $(g - 2)+$ oxidation state. To illustrate, $AlCl$ exists but $AlCl_3$ does not; $TiCl_3$ is less stable than $TiCl$.

The d -Transition Metals

► Oxides of most nonmetals are acidic, and oxides of most metals are basic (except those having high oxidation states).

The term “transition elements” denotes elements in the middle of the periodic table. They provide a transition between the “base formers” on the left and the “acid formers” on the right. The term applies to both the d - and f -transition elements (d and f atomic orbitals are being filled across this part of the periodic table). All are metals. We commonly use the term “transition metals” to refer to the d -transition metals.

3B	4B	5B	6B	7B	8B			1B	2B
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac	Rf	Db	Sg	Bh	Hs	Mt			

The d -transition metals are located between Groups 2A and 3A in the periodic table. Strictly speaking, a d -transition metal must have a partially filled set of d orbitals. Zinc, cadmium, and mercury (Group 2B) and their cations have completely filled sets of d orbitals, but they are often discussed with d -transition metals because their properties are similar. All of the other elements in this region have partially filled sets of d orbitals, except the 1B elements and palladium, which have completely filled sets. Some of the cations of these latter elements have partially filled sets of d orbitals.



Many transition metal ions are highly colored. These flasks contain (left to right) aqueous solutions of $Fe(NO_3)_3$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, and $Zn(NO_3)_2$. Colorless Zn^{2+} ions differ from the others by having completely filled $3d$ orbitals.

Table 27-6 Properties of Metals in the First Transition Series

Properties	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Melting point (°C)	1541	1660	1890	1850	1244	1535	1495	1453	1083	420
Boiling point (°C)	2831	3287	3380	2672	1962	2750	2870	2732	2567	907
Density (g/cm ³)	2.99	4.54	6.11	7.18	7.21	7.87	8.9	8.91	8.96	7.13
Atomic radius (Å)	1.62	1.47	1.34	1.25	1.29	1.26	1.25	1.24	1.28	1.34
Ionic radius, M ²⁺ (Å)	—	0.94	0.88	0.89	0.80	0.74	0.72	0.69	0.70	0.74
Electronegativity	1.3	1.4	1.5	1.6	1.6	1.7	1.8	1.8	1.8	1.6
E^0 (V) for $M^{2+}(aq) + 2e^- \longrightarrow M(s)$	-2.08*	-1.63	-1.2	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76
IE (kJ/mol) first	631	658	650	652	717	759	758	757	745	906
second	1235	1310	1414	1592	1509	1561	1646	1753	1958	1733

*For $Sc^{3+}(aq) + 3e^- \longrightarrow Sc(s)$.

27-8 General Properties

The following are general properties of transition elements.

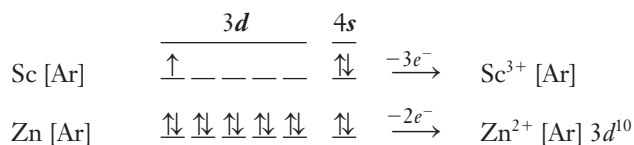
1. All are metals.
2. Most are harder and more brittle and have higher melting points, boiling points, and heats of vaporization than nontransition metals.
3. Their ions and their compounds are usually colored.
4. They form many complex ions (see Chapter 25).
5. With few exceptions, they exhibit multiple oxidation states.
6. Many of them are paramagnetic, as are many of their compounds.
7. Many of the metals and their compounds are effective catalysts.

Some properties of 3d-transition metals are listed in Table 27-6.

27-9 Oxidation States

Most transition metals exhibit more than one nonzero oxidation state. For the early transition metals, the *maximum* oxidation state is given by the metal's group number, but this is often not its most stable oxidation state (Table 27-7).

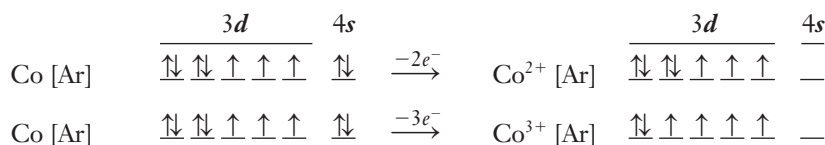
The outer *s* electrons lie outside the *d* electrons and are *always* the first ones lost in ionization. In the first transition series, scandium and zinc exhibit just one nonzero oxidation state. Scandium loses its two 4*s* electrons and its only 3*d* electron to form Sc^{3+} . Zinc loses its two 4*s* electrons to form Zn^{2+} .



► The early transition metals include Groups 3B to 5B, while the late transition metals are usually defined as Groups 8B, 1B, and 2B. The middle Groups 6B and 7B can often behave as either early or late transition metals in their chemistry.

► In the “building” of electron configurations by the Aufbau Principle, the outer *s* orbitals are occupied before the inner *d* orbitals (see Section 4-18).

Titanium and nickel also have only a single common nonzero oxidation state. All of the other 3d-transition metals exhibit at least two oxidation states in their compounds. For example, cobalt can form Co^{2+} and Co^{3+} ions.



Unless otherwise noted, all content on this page is © Cengage Learning.

Table 27-7 Common Nonzero Oxidation States of the 3d-Transition Metals*

3B Sc	4B Ti	5B V	6B Cr	7B Mn	8B Fe Co Ni			1B Cu	2B Zn
				+1				+1 <i>r</i>	
			+2	+2	+2 <i>r</i>	+2	+2	+2	+2
+3	+3 <i>r</i>	+3 <i>r</i>	+3	+3	+3	+3 <i>o</i>			
	+4	+4		+4 <i>o</i>					
		+5 <i>o</i>							
			+6 <i>o</i>						
				+7 <i>o</i>					

*Abbreviations: *o* = oxidizing agent; *r* = reducing agent.



James W. Mortenthaler

Pentaamminechlorocobalt(III) chloride, $[\text{Co}(\text{NH}_3)_5(\text{Cl})]\text{Cl}_2$, is a compound that contains cobalt in the +3 oxidation state (*left*). Hexaaquacobalt(II) chloride, $[\text{Co}(\text{OH}_2)_6]\text{Cl}_2$, contains cobalt in the +2 oxidation state (*right*).

The most common oxidation states of the 3d-transition elements are +2 and +3. The elements in the middle of each series exhibit more oxidation states than those to the left or right. As one moves down a group, higher oxidation states become more stable and more common (opposite of the trend for representative elements). This is because the *d* electrons are more effectively shielded from the nucleus as the group is descended and are therefore more easily lost or more readily available for sharing. For example, cobalt commonly exhibits the +2 and +3 oxidation states. Rh and Ir (just below Co) exhibit the common oxidation states +1 and +3. The +3 state is slightly more stable for Ir than for the more electronegative Rh.

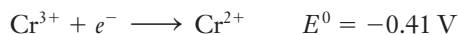
The oxides and hydroxides of lower oxidation states of a given transition metal are basic. Those containing intermediate oxidation states tend to be amphoteric, and those containing high oxidation states tend to be acidic. This is illustrated for the oxides and hydroxides of Cr in the next section.

27-10 Chromium Oxides, Oxyanions, and Hydroxides

Typical of the metals near the middle of a transition series, chromium shows several oxidation states. The most common are +2, +3, and +6 (Table 27-8).

Oxidation–Reduction

The most stable oxidation state of Cr is +3. Solutions of blue chromium(II) salts are easily air-oxidized to chromium(III).

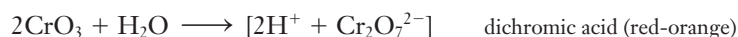


Chromium(VI) species are oxidizing agents. Basic solutions containing chromate ions, CrO_4^{2-} , are weakly oxidizing. Acidification produces the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, and chromium(VI) oxide, both powerful oxidizing agents.



Chromate–Dichromate Equilibrium

Red chromium(VI) oxide, CrO_3 , is the acid anhydride of two acids: chromic acid, H_2CrO_4 , and dichromic acid, $\text{H}_2\text{Cr}_2\text{O}_7$. Neither acid has been isolated in pure form, although chromate and dichromate salts are common. CrO_3 reacts with H_2O to produce strongly acidic solutions containing hydrogen ions and (predominantly) dichromate ions.



Charles Steele

Aqueous solutions of some compounds that contain chromium. (*Left to right*) Chromium(II) chloride (CrCl_2) is blue; chromium(III) chloride (CrCl_3) is green; potassium chromate (K_2CrO_4) is yellow; potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is orange.

Table 27-8 Some Compounds of Chromium

Our Love–Hate Relationship with Mercury

Zinc's "big" brothers are cadmium and mercury, both toxic materials very unlike zinc. Mercury, in particular, is one of the most toxic chemical elements. Anyone who eats fish has been warned about the potential for mercury poisoning, and the fierce regulatory debate about mercury emissions from coal-fired power plants is a nightly news staple. Yet, for many decades we've been using this element and its compounds in consumer products such as thermometers, light bulbs, and antiseptics, and paying dentists to fill our teeth with mercury amalgam. Why is it usable in some forms and applications, and deadly in others?

Most of mercury's common usages involve the metallic element. Although this is its least toxic form, it is not "safe" by any means, and when inhaled can cause headaches, tremors, and memory loss. Fluorescent lights and many streetlights use mercury-vapor emission as a light source. Compact fluorescent (CFL) bulbs designed for home use typically contain 1–5 mg of mercury. These bulbs present hazards when broken or commingled with regular trash, since waste incineration, if used, releases the mercury into the atmosphere. Several U.S. states have enacted laws regulating CFL bulb disposal and recycling. Similar concerns have rendered mercury thermometers the target of a phase-out effort by the Environmental Protection Agency. The thermometers you'll encounter in modern chemistry laboratory courses are more likely to contain a safer, brightly dyed red liquid such as kerosene.

Mercury-containing dental fillings have been in use since the early 19th century and have generated controversy about possible health risks since their introduction. Dental amalgam contains about 50% elemental mercury, alloyed with silver, tin, and copper. These fillings have largely been replaced by more aesthetically pleasing "composites," an organic polymer mixed with silica (SiO_2) or other inorganic component. The technology behind composite fillings has advanced to the point where their strength and longevity compete with those of amalgam. The U.S. Food and Drug Administration (FDA) considers amalgam fillings safe for adults and children over age six. However, they are now banned in Norway, Sweden, and Denmark. Most dentists in the United States have shifted to composite filling materials and are no longer using mercury amalgams.

Inorganic mercury compounds are more toxic than elemental mercury, and unsurprisingly, their commercial applications tend to involve killing things. Mercury(II) salts such as HgCl_2 , HgO , HgNO_3 , and HgI_2 have historically been used as antiseptics, fungicides, antibacterial agents, and disinfectants, in embalming, and in the treatment of hat felt

and animal skins. Mercury(I) chloride (calomel), which is not quite as nasty, is a common component of pH meter electrodes.

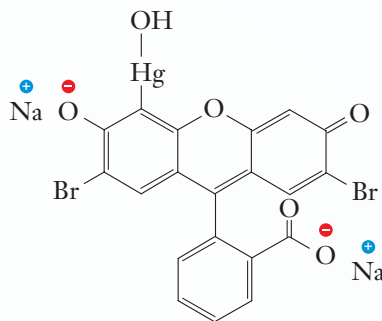
Even more deadly are organomercury compounds—particularly methylmercuries, which contain the CH_3Hg^+ ion. These compounds easily permeate gastrointestinal tract membranes to concentrate in blood and bind sulfur-containing groups in peptides. Alkylmercuries attack the central nervous system, accumulate in brain tissues, and are some of the most potent neurotoxins known. In a famous 1997 case of mercury poisoning, Dartmouth chemistry professor Karen Wetterhahn died from neurological disease after spilling a few drops of dimethylmercury, $(\text{CH}_3)_2\text{Hg}$, onto her latex glove during an experiment. The dimethylmercury easily penetrated the latex glove and was absorbed into her skin. Because of this, researchers that now work with organic mercury compounds wear gloves that are resistant to these dangerous compounds.

Methylmercuries are the source of the well-known concern about mercury poisoning from fish consumption. Bacteria present in sea and lake-bottom sediments can generate the CH_3Hg^+ ion from inorganic mercury compounds. It is then taken up by plankton and subsequently migrates up the marine food chain to bioaccumulate in fish, particularly larger, longer-living fish such as shark, king mackerel, and albacore tuna (who've had the most time to swim around eating smaller fish and collecting mercury). The current fear over potential links between childhood vaccines and autism also involves an organomercury, thimerosal, an ethylmercury-based preservative now almost entirely phased out of vaccine formulations. While numerous recent studies have failed to find any link between the use of thimerosal and autism rates, this controversy still persists in the nonscientific media.

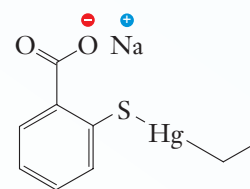
Your older relatives may remember having their childhood scrapes treated with Mercurochrome®, an organomercury formulation often referred to as "monkey blood." The active ingredient in this bright red antiseptic is a mercury(II) hydroxide salt, merbromin. You're unlikely to find it at your local pharmacy anymore due to the potential for mercury poisoning. Mercurochrome was removed from the FDA's "generally recognized as safe" list in the 1990s.

Mercury is a good example of the general technological problem also posed by other heavy metals—lead, cadmium, and thallium. These metals have important uses but are extremely damaging to living organisms and the environment. Arguments about the correct balance between their benefits and dangers are certain to continue for many years.

LISA SAUNDERS BAUGH



merbromin



thimerosal

KEY TERMS

Alkali metals Group 1A metals.

Alkaline earth metals Group 2A metals.

***d*-Transition metals** Metals that have partially filled sets of *d* orbitals; the B groups of the periodic table.

Diagonal similarities Chemical similarities of elements of Period 2 to elements of Period 3 one group to the right; especially evident toward the left of the periodic table.

Inert *s*-pair effect The tendency of the two outermost *s* electrons to remain nonionized or unshared in compounds; characteristic of the post-transition metals.

Post-transition metals Representative metals in the “*p* block.”

Representative metals Metals in the A groups in the periodic table; their outermost electrons are in *s* and *p* orbitals.

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

Properties and Chemistry of the Metals

- How do the acidities or basicities of metal oxides vary with oxidation numbers of the same metal?
- Discuss the general differences in electron configurations of representative elements and *d*-transition metals.
- Compare the extents to which the properties of successive elements across the periodic table differ for representative elements and *d*-transition metals. Explain.
- Compare the metals and nonmetals with respect to (a) number of outer-shell electrons, (b) electronegativities, (c) standard reduction potentials, and (d) ionization energies.
- Compare the melting points of the alkali metals (Group 1A) with the melting points of other metals. Compare the melting points of the alkali metals with each other and relate them to the locations of the elements on the periodic table.
- Define malleable and ductile.
- (a) What is the meaning of the statement, “alkali metals are corrosive”? (b) Are alkali metal ions corrosive? (c) Are alkali metal ions an important part of your diet?
- Compare the alkali metals with the alkaline earth metals with respect to (a) atomic radii, (b) densities, (c) first ionization energies, and (d) second ionization energies. Explain the comparisons.
- Summarize the chemical and physical properties of (a) the alkali metals, and (b) the alkaline earth metals.
- What changes are believed to occur within an atom of an alkali metal (Group 1A) when it reacts with a nonmetal?
- Which one of the alkaline earth metals (Group 2A) tends to form bonds that have the greatest amount of ionic character?
- (a) Compare and contrast the physical and chemical properties of the Group 1A metals with those of the Group 2A metals. (b) Compare the periodic trends of the two groups.
- Write the general outer-electron configurations for atoms of the 1A and 2A metals. What oxidation state(s) would you predict for these elements? What types of bonding would you expect in most of the compounds of these elements? Why?
- Write electron configurations (↑↓ notation) for (a) Ca, (b) Ca^{2+} , (c) Mg, (d) Mg^{2+} , (e) Sn, (f) Sn^{2+} , and (g) Sn^{4+} .
- Write electron configurations (↑↓ notation) for (a) Na, (b) Na^+ , (c) Sr, (d) Sr^{2+} , (e) Al, (f) Al^{3+} , and (g) Ga^{3+} .
- Are the elements in Groups 1A and 2A found in the free state in nature? What are the primary sources for these elements?
- Describe some uses for (a) lithium and its compounds, and (b) sodium and its compounds.
- Where do the metals of Groups 1A and 2A fall with respect to H_2 in the activity series? What does this tell us about their reactivities with water and acids?



Charles D. Winters

K added to water

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

20. Describe some uses for (a) calcium and its compounds, and (b) magnesium and its compounds.
21. Write general equations for reactions of alkali metals with (a) hydrogen, (b) sulfur, and (c) ammonia. Represent the metal as M.
22. Write general equations for reactions of alkali metals with (a) water, (b) phosphorus, and (c) halogens. Represent the metal as M and the halogen as X.
23. Write general equations for reactions of alkaline earth metals with (a) hydrogen, (b) sulfur, and (c) ammonia. Represent the metal as M.
24. Write general equations for reactions of alkaline earth metals with (a) water, (b) phosphorus, and (c) chlorine. Represent the metal as M.
25. Just as lithium (Li) and its compounds are more like magnesium (Mg) and its compounds than they are like other elements in the lithium family (Group 1A), beryllium (Be) is more like aluminum (Al) than it is like the other elements in Group 2A, and boron (B) is more like silicon (Si) than it is like the other elements in Group 3A. What are some ways in which beryllium is similar to aluminum? What are some ways in which boron is similar to silicon?
26. Give some illustrations of diagonal similarities in the periodic table, and explain each.
27. What is hydration energy? How does it vary for cations of the alkali metals?
28. How do hydration energies vary for cations of the alkaline earth metals?
29. How do the standard reduction potentials of the alkali metal cations vary? Why?
30. How do the standard reduction potentials of the alkaline earth metal cations vary? Why?
31. Why are the standard reduction potentials of lithium and beryllium out of line with respect to group trends?
32. Calculate ΔH° values at 25°C for the reactions of 1 mol of each of the following metals with stoichiometric quantities of water to form metal hydroxides and hydrogen: (a) Li, (b) K, and (c) Ca. Rationalize the differences in these values.
33. How are the *d*-transition metals distinguished from other elements?
34. What are the general properties of the *d*-transition metals?
35. Why are trends in variations of properties of successive *d*-transition metals less regular than trends among successive representative elements?
36. Write out the electron configurations for the following species: (a) Sc, (b) Fe, (c) Cu, (d) Zn^{2+} , (e) Cr^{3+} , (f) Ni^{2+} , (g) Ag, and (h) Ag^+ .
37. Why do copper and chromium atoms have “unexpected” electron configurations?
38. Discuss the similarities and differences among elements of corresponding A and B groups of the periodic table, 3A and 3B for example.
39. Write electron configurations for the common oxidation states of (a) silver, and (b) gold.
40. What two properties listed in Table 27-1 suggest that the Group 1A metals are very unlikely to occur as free metals?
41. Copper exists in the +1, +2, and +3 oxidation states. Which is the most stable? Which would you expect to be a strong oxidizing agent, and which would you expect to be a strong reducing agent?
42. For a given transition metal in different oxidation states, how does the acidic character of its oxides increase? How do ionic and covalent characters vary? Characterize a series of metal oxides as examples.
43. For different transition metals in the same oxidation state in the same group (vertical column) of the periodic table, how do covalent character and acidic character of their oxides vary? Why? Cite evidence for the trends.
44. Chromium(VI) oxide is the acid anhydride of which two acids? Write their formulas. What is the oxidation state of the chromium in these acids?
45. Use the data in Tables 27-1 and 27-3 to explain your answers to the following questions. (a) What is the trend of ease of formation of 1+ ions by the Group 1A metals? (b) What is the trend of ease of formation of 1+ ions by the Group 2A metals? (c) What is the trend of ease of formation of 2+ ions by the Group 2A metals? (d) Which metals more easily form 1+ ions—those in Group 1A or in Group 2A? (e) Which metals more easily form 2+ ions—those in Group 1A or in Group 2A?
46. In Appendix H, look up the solubility product constants for $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, and $\text{Ba}(\text{OH})_2$. The solubility product constant for $\text{Be}(\text{OH})_2$ is about 7×10^{-22} . Calculate the $[\text{OH}^-]$ and the pOH of saturated solutions of each of these compounds. Based upon this information, which of these compounds are strong bases? Which compound can form solutions that are slightly basic, but not enough to call it a strong base? Which one cannot produce more hydroxide ions than the autoionization of water? Relate the base strengths to the relative locations of the metals on the periodic table.
47. Among the *d*-transition metals, the elements of Group 1B (Cu, Ag, and Au) are sometimes referred to as the “coinage metals.” Why? What properties do they have that make them particularly useful for this purpose?
48. What is the mass percent of chromium in the chloride salt of $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$?

Conceptual Exercises

49. Some of the oxides of the transition metals are amphoteric. (a) What is meant by the term amphoteric? (b) Identify five oxides that are amphoteric, five oxides that are basic, and five oxides that are acidic.
50. Calcium carbonate is a very common compound on this planet. Name five common items that are composed primarily of calcium carbonate.
51. Magnesium and some of the magnesium alloys will burn if heated to a high enough temperature. Some magnesium alloys are used in construction and may have to be welded at a high temperature. Suggest techniques or requirements for welding these alloys so that they do not ignite.

52. Some mental disorders are treated with medications that contain lithium salts. Why is pure lithium unsuitable for such purposes?



Charles D. Winters

Pure lithium

53. Gallium thermometers are high-temperature thermometers. (a) Why can't they be used near room temperature? (b) Propose a reason why mercury thermometers cannot be used to measure temperatures in the upper range of gallium thermometers.



Charles D. Winters

Pure gallium

54. How are the maximum oxidation states for the metals in Groups 3B through 7B related to the locations of the elements on the periodic table?
55. Describe the change in the acid/base character of oxides of the same *d*-transition metal as the oxidation state of the metal changes from its minimum value to its maximum value.

Building Your Knowledge

56. How many grams of Co_3O_4 (a mixed oxide, $\text{CoO} \cdot \text{Co}_2\text{O}_3$) must react with excess aluminum to produce 190. g of metallic cobalt, assuming 67.5% yield?



57. Calculate ΔH° , ΔS° , and ΔG° for the reaction of 1 mol of Na with water to form aqueous NaOH and hydrogen.
58. Calculate ΔH° , ΔS° , and ΔG° for the reaction of 1 mol of Rb with water to form aqueous RbOH and hydrogen. Compare the spontaneity of this reaction with that in Exercise 57.

59. What is the ratio of $[\text{Cr}_2\text{O}_7^{2-}]$ to $[\text{CrO}_4^{2-}]$ at 25°C in a solution prepared by dissolving 1.5×10^{-3} mol of sodium chromate, Na_2CrO_4 , in enough of an aqueous solution buffered at $\text{pH} = 2.00$ to produce 235 mL of solution?
60. An unknown compound is known to be the carbonate of either a Group 1A or a Group 2A element. Repeated heating of 14.78 grams of the unknown produced a total of 4.48 L of carbon dioxide at 0°C and 1 atm pressure (101 kPa). Calculate the number of moles of CO_2 produced, and identify the unknown compound.
61. Write the balanced formula unit, total ionic equations, and net ionic equations for the following. Include state designations in your answers—(s), (aq), etc. (a) The reaction of beryllium with a solution of sodium hydroxide. (b) The reaction of calcium with water. (c) The reaction of aluminum with sodium hydroxide.
62. Write the balanced formula unit, total ionic equations, and net ionic equations for the following. Include state designations in your answers—(s), (aq), etc. (a) The reaction of magnesium with steam. (b) The reaction of rubidium with water. (c) The reaction of chromium(III) hydroxide with a solution of sodium hydroxide.

Beyond the Textbook

NOTE: Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.

63. Open www.saltinstitute.org or a site dealing with the salt industry. (a) Name three states within the United States that have rock salt mines. (b) Of the sodium chloride mined (solid or solution), what percent of it is used to de-ice roads? (c) Name the two important products in the chemical industries that depend upon sodium chloride as a starting material.
64. Water- and air-sensitive chemicals are often stored and handled inside a "glove box" filled with a dry, inert gas, typically nitrogen or argon. Which of these two gases would be the better choice for a glove box used to handle lithium metal? Why? Are there other metals with the same problem?
65. Use the Environmental Protection Agency's web site (<http://www.epa.gov>) or an internet search engine (such as <http://www.google.com>) to research information on lead poisoning. (a) What is the greatest source of concern for children's lead poisoning in homes? What are other sources of exposure? (b) What year was the main usage of lead in (a) banned by the federal government? (c) What two metal ions, when present in food, help protect the body from absorbing lead? Why might this be?



Some Nonmetals and Metalloids

28



The tower in the background is part of the Frasch process that pumps molten sulfur (*dark orange*) from underground deposits. After it cools, it forms bright yellow solid sulfur. The workers are wearing respirators to protect them from the small amounts of SO_2 that form when the hot molten sulfur reacts with oxygen in the air.

© Robert Wallis/Corbis

OUTLINE

The Noble Gases (Group 8A)

- 28-1 Occurrence, Uses, and Properties
- 28-2 Xenon Compounds

The Halogens (Group 7A)

- 28-3 Properties
- 28-4 Occurrence, Production, and Uses
- 28-5 Reactions of the Free Halogens
- 28-6 The Hydrogen Halides and Hydrohalic Acids
- 28-7 The Oxoacids (Ternary Acids) of the Halogens

Sulfur, Selenium, and Tellurium

- 28-8 Occurrence, Properties, and Uses
- 28-9 Reactions of Group 6A Elements
- 28-10 Hydrides of Group 6A Elements
- 28-11 Group 6A Oxides
- 28-12 Oxoacids of Sulfur

Nitrogen and Phosphorus

- 28-13 Occurrence of Nitrogen
- 28-14 Hydrogen Compounds of Nitrogen
- 28-15 Nitrogen Oxides
- 28-16 Some Oxoacids of Nitrogen and Their Salts
- 28-17 Phosphorus

Silicon

- 28-18 Silicon and the Silicates

OBJECTIVES

After you have studied this chapter, you should be able to

- ▶ Describe the occurrence and use of the noble gases
- ▶ Describe compounds of the noble gases
- ▶ Describe the occurrence and production of the halogens
- ▶ Describe some important reactions and compounds of the halogens
- ▶ Describe the occurrence and production of sulfur, selenium, and tellurium
- ▶ Describe some important reactions and compounds of the heavier Group 6A nonmetals
- ▶ Describe the occurrence and production of nitrogen and phosphorus
- ▶ Describe some important reactions of nitrogen and phosphorus
- ▶ Describe the occurrence and importance of silicon
- ▶ Describe a few important compounds of silicon

Only about 20% of the elements are classified as nonmetals. With the exception of H, they are in the upper right-hand corner of the periodic table. In this chapter we shall consider the chemistry and properties of nonmetals and metalloids that illustrate group trends and individuality of elements within groups of nonmetals.

		7A		8A	
				He	
		N		F Ne	
		Si P		S Cl Ar	
				Se Br Kr	
		Te		I Xe	
		At		Rn	

The Noble Gases (Group 8A)

28-1 Occurrence, Uses, and Properties

▶ Radon is continually produced in small amounts in the uranium radioactive decay sequence (see Section 22-11). Radon gas is so unreactive that it eventually escapes from the soil. Measurable concentrations of radon, a radioactive gas, have been observed in basements of many dwellings. See the Chemistry in Use essay "Household Radon Exposure and Lung Cancer" in Chapter 22.

▶ A pressure of about 26 atmospheres is required to solidify He at 0.001 K.

The noble gases are very low boiling gases. Except for radon, they can be isolated by fractional distillation of liquefied air. Radon is collected from the radioactive disintegration of radium salts. Table 28-1 gives the percentage of each noble gas in the atmosphere.

Helium is produced in the United States from some natural gas fields. This source was discovered in 1905 by H. P. Cady and D. F. McFarland at the University of Kansas, when they were asked to analyze a nonflammable component of natural gas from a Kansas gas well. Uses of the noble gases are summarized in Table 28-2.

The noble gases are colorless, tasteless, and odorless. In the liquid and solid states, the only forces of attraction among the atoms are very weak dispersion forces. Polarizability and interatomic interactions increase with increasing atomic size, and so melting and boiling points increase with increasing atomic number. The attractive forces among He atoms are so small that He remains liquid at 1 atmosphere pressure, even at a temperature of 0.001 K.

Table 28 -1 Percentages (by Volume) of Noble Gases in the Atmosphere

He	Ne	Ar	Kr	Xe	Rn
0.0005%	0.015%	0.94%	0.00011%	0.000009%	≈0%

Table 28-2 Uses of the Noble Gases

Noble Gas	Use	Useful Properties or Reasons
helium	1. Filling of observation balloons and other lighter-than-air craft 2. He/O₂ mixtures, rather than N₂/O₂, for deep-sea breathing 3. Diluent for gaseous anesthetics 4. He/O₂ mixtures for respiratory patients 5. Heat transfer medium for nuclear reactors 6. Industrial applications, such as inert atmosphere for welding easily oxidized metals 7. Liquid He used to maintain very low temperatures in research (cryogenics)	Nonflammable; 93% of lifting power of flammable hydrogen Low solubility in blood; prevents nitrogen narcosis and “bends” Nonflammable; nonreactive Low density; flows easily through restricted passages Transfers heat readily; does not become radioactive; chemically inert Chemically inert Extremely low boiling point
neon	Neon signs	Even at low Ne pressure, moderate electric current causes bright orange-red glow; can be modified by colored glass or mixing with Ar or Hg vapor
argon	1. Inert atmosphere for welding 2. Filling incandescent lightbulbs	Chemically inert Inert; inhibits vaporization of tungsten filament and blackening of bulbs
krypton	Airport runway and approach lights	Gives longer life to incandescent lights than Ar, but more expensive
xenon	Xe and Kr mixture in high-intensity, short-exposure photographic flash tubes	Both have fast response to electric current
radon	Radiotherapy of cancerous tissues	Radioactive

28-2 Xenon Compounds

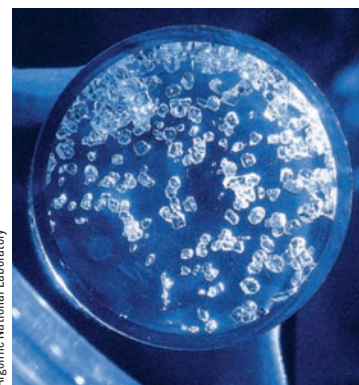
Until the early 1960s, chemists believed that the Group 8A elements would not combine chemically with any elements. In 1962, Neil Bartlett (1932–2008) and his research group at the University of British Columbia were studying the powerful oxidizing agent PtF₆. They accidentally prepared and identified O₂⁺PtF₆[−] by reaction of oxygen with PtF₆. Bartlett reasoned that xenon also should be oxidized by PtF₆ because the first ionization energy of O₂ (1.31×10^3 kJ/mol) is slightly larger than that of xenon (1.17×10^3 kJ/mol). He obtained a red crystalline solid initially believed to be Xe⁺PtF₆[−] but now known to be a more complex compound.

Since Bartlett's discovery, many other noble gas compounds have been made. All involve very electronegative elements. Most are compounds of Xe, and the best characterized compounds are xenon fluorides. Oxygen compounds are also well known. Reaction of Xe with F₂, an extremely strong oxidizing agent, in different stoichiometric ratios produces xenon difluoride, XeF₂; xenon tetrafluoride, XeF₄; and xenon hexafluoride, XeF₆, all colorless crystals (Table 28-3).

All the xenon fluorides are formed in exothermic reactions. They are reasonably stable, with Xe—F bond energies of about 125 kJ/mol of bonds. For comparison, strong covalent bond energies range from about 170 to 500 kJ/mol, whereas bond energies of hydrogen bonds are typically less than 40 kJ/mol.

► The noble gases are often called the rare gases. They were formerly called the “inert gases” because it was incorrectly thought that they could not enter into chemical combination.

► Oxygen is second only to fluorine in electronegativity.



Crystals of the noble gas compound xenon tetrafluoride, XeF₄.

The Halogens (Group 7A)

The elements of Group 7A are known as **halogens** (Greek, “salt formers”). The term “**halides**” is used to describe their binary compounds with less electronegative elements and indicates that each halogen exists in the −1 oxidation state. The heaviest halogen, as-

Table 28-3 Xenon Fluorides

Compound	Preparation (Molar ratio Xe : F ₂)	Reaction Conditions	e ⁻ Pairs Around Xe	Xe Hybridization, Molecular Geometry*
XeF ₂	1 : 1–3	400°C or irradiation or elec. discharge	5	sp ³ d, linear
XeF ₄	1 : 5	Same as for XeF ₂	6	sp ³ d ² , square planar
XeF ₆	1 : 20	300°C and 60 atm or elec. discharge	7	sp ³ d ³ (?), exact geometry undetermined

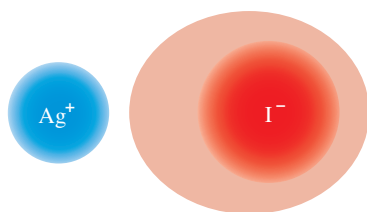
*See Tables 8-3 and 8-4.

tatine, is an artificially produced element of which only short-lived radioactive isotopes are known.

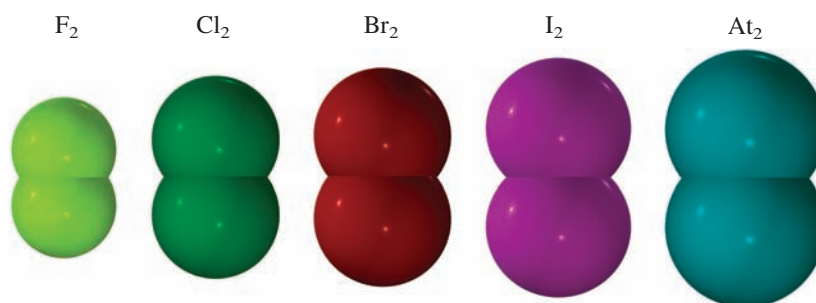
28-3 Properties

The elemental halogens exist as diatomic molecules containing single covalent bonds. Properties of the halogens show obvious trends (Table 28-4). Their high electronegativities indicate that they attract electrons strongly. Many binary compounds that contain a metal and a halogen are ionic.

The small fluoride ion (radius = 1.19 Å) is not easily polarized (distorted) by cations, whereas the large iodide ion (radius = 2.06 Å) is. As a result, compounds containing I⁻ ions show greater covalent character than those containing F⁻ ions. The properties of Cl⁻ and Br⁻ ions are intermediate between those of F⁻ and I⁻.



The diffuse valence shell cloud of the I⁻ ion is easily polarized by the small Ag⁺ ion.

**Table 28-4** Properties of the Halogens

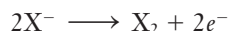
Property	F	Cl	Br	I	At
Physical state (25°C, 1 atm)	gas	gas	liquid	solid	solid
Color	pale yellow	yellow-green	red-brown	violet (g); black (s)	—
Atomic radius (Å)	0.72	1.00	1.14	1.33	1.40
Ionic radius (X ⁻) (Å)	1.19	1.67	1.82	2.06	—
Outer shell e ⁻	2s ² 2p ⁵	3s ² 3p ⁵	4s ² 4p ⁵	5s ² 5p ⁵	6s ² 6p ⁵
First ionization energy (kJ/mol)	1681	1251	1140	1008	890
Electronegativity	4.0	3.0	2.8	2.5	2.1
Melting point (°C, 1 atm)	-220	-101	-7.1	114	—
Boiling point (°C, 1 atm)	-188	-35	59	184	—
X—X bond energy (kJ/mol)	155	242	193	151	—

Unless otherwise noted, all content on this page is © Cengage Learning.

The chemical properties of the halogens resemble one another more closely than do those of elements in any other periodic group, with the exception of the noble gases and possibly the Group 1A metals. But their physical properties differ significantly. Melting and boiling points of the halogens increase from F_2 to I_2 . This follows their increase in size (see figure on previous page) and increase in ease of polarization of outer-shell electrons by adjacent nuclei, resulting in greater intermolecular attractive (dispersion) forces. All halogens except astatine are decidedly nonmetallic. They show the -1 oxidation number in most of their compounds. With the exception of fluorine, they also exhibit oxidation numbers of $+1$, $+3$, $+5$, and $+7$.

28-4 Occurrence, Production, and Uses

The halogens are so reactive that they do not occur as free elements in nature. The most abundant sources of halogens are halide salts. A primary source of iodine is $NaIO_3$. The halogens are obtained by oxidation of the halide ions.



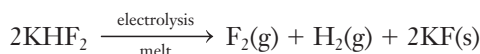
The order of increasing ease of oxidation is $F^- < Cl^- < Br^- < I^- < At^-$.

► We often represent a halogen atom as X, without specifying a particular halogen.

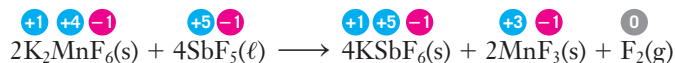
Fluorine

Fluorine occurs in large quantities in the minerals *fluorspar* or *fluorite*, CaF_2 ; *cryolite*, Na_3AlF_6 ; and *fluorapatite*, $Ca_5(PO_4)_3F$. It also occurs in small amounts in seawater, teeth, bones, and blood. F_2 is such a strong oxidizing agent that it has not been produced by *direct* chemical oxidation of the extremely stable F^- ions. The pale yellow gas is prepared by electrolysis of a molten mixture of $KF + HF$, or KHF_2 , in a Monel metal cell. This must be done under anhydrous conditions because H_2O is more readily oxidized than F^- .

► Monel metal is an alloy of Ni, Cu, Al, and Fe. It is resistant to attack by hydrogen fluoride.



In 1986, Carl O. Christe discovered that the strong Lewis acid SbF_5 displaces the weaker Lewis acid MnF_4 from the hexafluoromanganate(IV) ion, $[MnF_6]^{2-}$. MnF_4 is thermodynamically unstable, and it decomposes into MnF_3 and F_2 . Christe heated a mixture of potassium hexafluoromanganate(IV) and antimony(V) fluoride in a passivated Teflon–stainless steel container at $150^\circ C$ for 1 hour. He obtained elemental F_2 in greater than 40% yield. The overall reaction may be represented as



Fluorine is used as a fluorinating agent. Many fluorinated organic compounds are stable and nonflammable. They are used as refrigerants, lubricants, plastics (such as Teflon), insecticides, and, until recently, aerosol propellants. Stannous fluoride, SnF_2 , is used in toothpaste.

► The reactions of F_2 with other elements are dangerous because of the vigor with which F_2 oxidizes other substances. They must be carried out with *extreme caution*!

Chlorine

Chlorine (Greek *chlōros*, “green”) occurs in abundance in $NaCl$, KCl , $MgCl_2$, and $CaCl_2$ in saltwater and in salt beds. It is also present as HCl in gastric juices. The toxic, yellowish green gas is prepared commercially by electrolysis of concentrated aqueous $NaCl$, in which industrially important H_2 and caustic soda ($NaOH$) are also produced (see Section 21-4). More than 23 billion pounds of chlorine was produced in the United States in 2010.

Chlorine is used to produce many commercially important products. Tremendous amounts of it are used in extractive metallurgy and in chlorinating hydrocarbons to produce a variety of compounds (such as polyvinyl chloride, a plastic). Chlorine is present as Cl_2 , $NaClO$, $Ca(ClO)_2$, or $Ca(ClO)Cl$ in household bleaches, as well as in bleaches for wood pulp and textiles. Under carefully controlled conditions, Cl_2 is used to kill bacteria in public water supplies.



Chlorides occur in salt beds.

Bromine

Bromine (Greek *bromos*, “stench”) is less abundant than fluorine and chlorine. In the elemental form, it is a dense, freely flowing, corrosive, dark-red liquid with a brownish red vapor at 25°C. It occurs mainly in NaBr, KBr, MgBr₂, and CaBr₂ in saltwater, underground salt brines, and salt beds. The major commercial source of bromine is deep brine wells in Arkansas that contain up to 5000 parts per million (0.5%) of bromide.

Bromine is used in the production of silver bromide for light-sensitive eyeglasses and photographic film; in the production of sodium bromide, a mild sedative; in methyl bromide, CH₃Br, a soil fumigant that contributes to the destruction of the ozone layer; and in brominated organic compounds that are used as flame retardants.

Iodine

Iodine (Greek *iodos*, “purple”) is a violet-black crystalline solid with a metallic luster. It exists in equilibrium with a violet vapor at 25°C. The element can be obtained from dried seaweed or shellfish, or from NaIO₃ impurities in Chilean nitrate (NaNO₃) deposits. It is contained in the growth-regulating hormone thyroxine, produced by the thyroid gland. “Iodized” table salt is about 0.02% KI in NaCl, which helps prevent goiter, a condition in which the thyroid enlarges. Iodine has been used as an antiseptic and germicide in the form of tincture of iodine, a solution in alcohol. An aqueous solution of iodine that does not sting when applied to open wounds is based on an iodine complex of polyvinylpyrrolidone. This is called povidone-iodine; Betadine is a specific brand often used in hospitals.

The preparation of iodine involves reduction of iodate ion from NaIO₃ with sodium hydrogen sulfite, NaHSO₃.



Iodine is then purified by sublimation (see Figure 13-16).

28-5 Reactions of the Free Halogens

The free halogens react with most other elements and many compounds. For example, all the Group 1A metals react with all the halogens to form simple binary ionic compounds (see Section 7-2).

General Reaction	Remarks
$n\text{X}_2 + 2\text{M} \longrightarrow 2\text{MX}_n$	All X ₂ with most metals (most vigorous reaction with F ₂ and Group 1A metals)
$\text{X}_2 + n\text{X}'_2 \longrightarrow 2\text{XX}'_n$	Formation of interhalogens ($n = 1, 3, 5, \text{ or } 7$); X is larger than X'
$\text{X}_2 + \text{H}_2 \longrightarrow 2\text{HX}$	With all X ₂
$3\text{X}_2 + 2\text{P} \longrightarrow 2\text{PX}_3$	With all X ₂ , and with As, Sb, Bi replacing P
$5\text{X}_2 + 2\text{P} \longrightarrow 2\text{PX}_5$	Not with I ₂ ; also Sb $\longrightarrow$ SbF ₅ , SbCl ₅ ; As $\longrightarrow$ AsF ₅ ; Bi $\longrightarrow$ BiF ₅
$\text{X}_2 + \text{H}_2\text{S} \longrightarrow \text{S} + 2\text{HX}$	With all X ₂
$\text{X}'_2 + 2\text{X}^- \longrightarrow 2\text{X}'^- + \text{X}_2$	F ₂ $\longrightarrow$ Cl ₂ , Br ₂ , I ₂ Cl ₂ $\longrightarrow$ Br ₂ , I ₂ Br ₂ $\longrightarrow$ I ₂

The most vigorous reactions are those of F₂, which usually oxidizes other species to their highest possible oxidation states. Iodine is only a mild oxidizing agent (I⁻ is a mild reducing agent) and usually does not oxidize substances to high oxidation states. Consider the following reactions of halogens with two metals that exhibit variable oxidation numbers.



Charles D. Winters

Bromine is a dark red, volatile liquid.



Cengage Learning/Charles Steele

Iodine reacts with starch (as in this potato) to form a deep-blue complex substance.



Cengage Learning/Charles Steele

Bromine reacts with powdered antimony so vigorously that the flask vibrates.

With Fe		With Cu	
$2\text{Fe} + 3\text{F}_2$	$\longrightarrow 2\text{FeF}_3$ (only)		
$2\text{Fe} + 3\text{Cl}_2$ (excess)	$\longrightarrow 2\text{FeCl}_3$	$\text{Cu} + \text{X}_2 \longrightarrow \text{CuX}_2$ (X = F, Cl, Br)	
$\text{Fe} + \text{Cl}_2$ (lim. amt.)	$\longrightarrow \text{FeCl}_2$		
$\text{Fe} + \text{I}_2$	$\longrightarrow \text{FeI}_2$ (only)	$2\text{Cu} + \text{I}_2 \longrightarrow 2\text{CuI}$ (only)	
$\text{Fe}^{3+} + \text{I}^-$	$\longrightarrow \text{Fe}^{2+} + \frac{1}{2}\text{I}_2$	$\text{Cu}^{2+} + 2\text{I}^- \longrightarrow \text{CuI} + \frac{1}{2}\text{I}_2$	

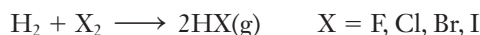


Iron and chlorine react to form iron(III) chloride, FeCl_3 .

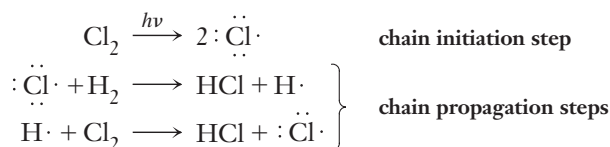
28-6 The Hydrogen Halides and Hydrohalic Acids

The hydrogen halides are colorless gases that dissolve in water to give acidic solutions called hydrohalic acids. The gases have piercing, irritating odors. The abnormally high melting and boiling points of HF are due to its very strong hydrogen bonding (Figure 13-5).

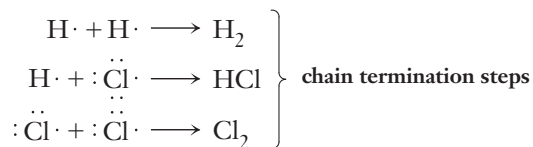
Hydrogen halides can be prepared by combination of the elements.



The reaction with F_2 to produce HF is explosive and very dangerous. The reaction producing HCl does not occur significantly in the dark, but occurs rapidly by a photochemical **chain reaction** when the mixture is exposed to light. Light energy is absorbed by Cl_2 molecules, which break apart into very reactive chlorine atoms, which have unpaired electrons (**radicals**). These subsequently attack H_2 molecules to produce HCl molecules and hydrogen atoms (also radicals). The hydrogen radicals, in turn, attack Cl_2 molecules to form HCl molecules and chlorine radicals, and the process continues.

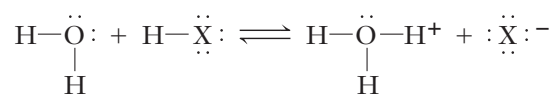


This chain reaction continues as long as there is a significant concentration of radicals. **Chain termination steps** eliminate two radicals and can eventually terminate the reaction.

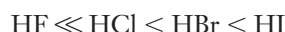


The reaction of H_2 with Br_2 is also a photochemical reaction. The reaction of H_2 with I_2 is very slow, even at high temperatures and with illumination.

All hydrogen halides react with H_2O to produce *hydrohalic acids* that ionize.



The order of increasing acid strengths of the aqueous hydrohalic acids is



► Concentrated anhydrous HF is considered a “superacid” due to the reaction:



This is used in some petroleum refineries to convert alkenes and isobutane into higher molecular-weight branched hydrocarbons that have higher octane ratings for gasoline.

► With excess hydrofluoric acid, H_2SiF_6 is also produced.

► In HOF, the oxidation states are $\text{F} = -1$, $\text{H} = +1$, $\text{O} = 0$.

► These reactions all involve *disproportionation* of the halogen.

► Some solid household bleaches are $\text{Ca}(\text{ClO})\text{Cl}$. This is prepared by reaction of Cl_2 with $\text{Ca}(\text{OH})_2$.

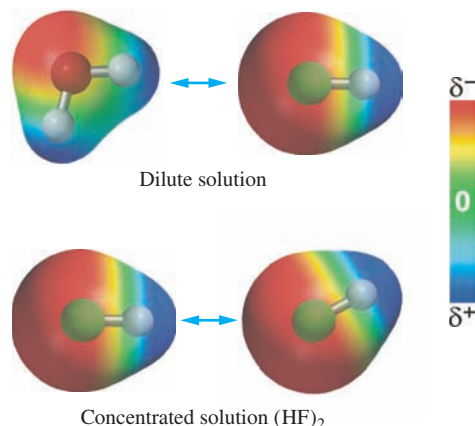
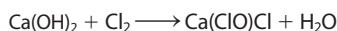


Figure 28-1 Hydrogen bonding (blue arrows) in dilute and concentrated aqueous solutions of hydrofluoric acid, HF.

The ionization reaction is essentially complete for dilute aqueous solutions of HCl, HBr, and HI. In dilute aqueous solutions, HF is a weak acid ($K_a = 7.2 \times 10^{-4}$). In concentrated solutions, more acidic dimeric $(\text{HF})_2$ units are present (Figure 28-1). They ionize as follows.



The only acid used in industry to a greater extent than HCl is H_2SO_4 . Hydrochloric acid is used in the production of metal chlorides, dyes, and many other commercially important products. It is also used on a large scale to dissolve metal oxide coatings from iron and steel prior to galvanizing or enameling.

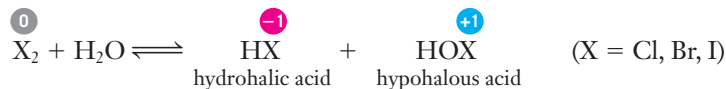
Hydrofluoric acid is used in the production of fluorine-containing compounds and for etching glass. The acid reacts with silicates, such as calcium silicate, CaSiO_3 , in the glass to produce a very volatile and thermodynamically stable compound, silicon tetrafluoride, SiF_4 .



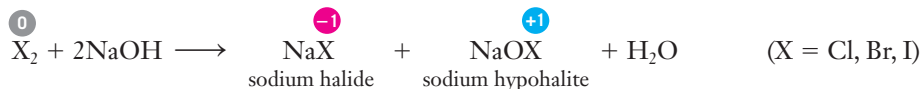
28-7 The Oxoacids (Ternary Acids) of the Halogens

Table 28-5 lists the known oxoacids of the halogens, their sodium salts, and some trends in properties. Only three oxoacids, HClO_4 , HIO_3 , and H_5IO_6 , have been isolated in anhydrous form. The others are known only in aqueous solution. In all these acids, the H is bonded through an O.

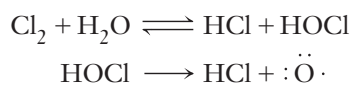
The only oxoacid of fluorine that has been prepared is unstable hypofluorous acid, HOF. Aqueous *hypohalous acids* (except HOF) can be prepared by reaction of free halogens (Cl_2 , Br_2 , I_2) with cold water. The smaller the halogen, the farther to the right the equilibrium lies.



Hypohalite salts can be prepared by reactions of the halogens with *cold* dilute bases.



The hypohalites are used as bleaching agents. Sometimes Cl_2 is used as a bleach or as a disinfectant, as in public water supplies. It reacts slowly with H_2O to form HCl and HOCl. The hypochlorous acid then decomposes into HCl and O radicals, which kill bacteria.



These oxygen radicals are very strong oxidizing agents. They are the effective bleaching and disinfecting agent in aqueous solutions of Cl_2 or hypochlorite salts.

Table 28-5 Halogen Oxoacids and Their Salts

Halogen	Oxidation State	Acid	Name	Thermal Stability of Acid Strength	Sodium Salt	Name	Thermal Stability	Hydrolysis of Anion
X = F, Cl, Br, I	+1	HXO	hypohalous acid	Increase ↓	NaXO	sodium hypohalite	Increases ↓	Increases ↑
X = Cl, Br	+3	HXO ₂	halous acid		NaXO ₂	sodium halite		
X = Cl, Br, I	+5	HXO ₃	halic acid		NaXO ₃	sodium halate		
X = F, Cl, Br, I	+7	HXO ₄	perhalic acid		NaXO ₄	sodium perhalate		
X = I only	+7	H ₅ XO ₆	orthoperiodic acid		Na ₅ IO ₆	sodium orthoperiodate		

Perchloric acid is the strongest of all common acids with respect to ionization. Hot, concentrated perchloric acid is a very strong oxidizing agent that can explode in the presence of reducing agents. Cold, dilute perchloric acid is only a weak oxidizing agent.

Sulfur, Selenium, and Tellurium

28-8 Occurrence, Properties, and Uses

Each Group 6A element is less electronegative than its neighboring halogen. Oxygen and sulfur are clearly nonmetallic, but selenium is less so. Tellurium is usually classified as a metalloid and forms metal-like crystals. Its chemistry is mostly that of a nonmetal. Polonium is a metal. All 29 isotopes of polonium are radioactive.

Irregularities in the properties of elements within a given family increase toward the middle of the periodic table. There are larger differences in the properties of the Group 6A elements than in the properties of the halogens. The properties of elements in the *second period* usually differ significantly from those of other elements in their families because second-period elements have no low-energy *d* orbitals. So, the properties of oxygen are not very similar to those of the other Group 6A elements (Table 28-6). The maximum number of electrons that O can have in its valence shell is eight. The heavier Group 6A elements—S, Se, Te, and Po—have *d* orbitals in their valence shells; one or more of these *d* orbitals can accommodate additional electrons to form up to six bonds. Thus, each of the Group 6A elements except O can bond covalently to as many as six other atoms.

Sulfur

Sulfur makes up about 0.05% of the earth's crust. It was one of the elements known to the ancients. It was used by the Egyptians as a yellow coloring, and it was burned in some religious ceremonies because of the unusual odor it produced; it is the “brimstone” of the Bible. Alchemists tried to incorporate its “yellowness” into other substances to produce gold.

Sulfur occurs as the free element—predominantly S₈ molecules—and in metal sulfides such as galena, PbS; iron pyrite, FeS₂; and cinnabar, HgS. To a lesser extent, it occurs as metal sulfates such as barite, BaSO₄, and gypsum, CaSO₄ · 2H₂O, and in volcanic gases as H₂S and SO₂.

Sulfur is found in much naturally occurring organic matter, such as petroleum and coal. Its presence in fossil fuels causes environmental and health problems because many sulfur-containing compounds burn to produce sulfur dioxide, an air pollutant.

► The *d* orbitals do not occur until the third energy level.



Native sulfur. Elemental sulfur is deposited at the edges of some hot springs and geysers. This formation surrounds Emerald Lake in Yosemite National Park.

Unless otherwise noted, all content on this page is © Cengage Learning.

Table 28-6 Some Properties of Group 6A Elements

Property	O	S	Se	Te	Po
Physical state (1 atm, 25°C)	gas	solid	solid	solid	solid
Color	colorless (very pale blue)	yellow	red-gray to black	brass-colored, metallic luster	—
Outermost electrons	$2s^22p^4$	$3s^23p^4$	$4s^24p^4$	$5s^25p^4$	$6s^26p^4$
Melting point (1 atm, °C)	−218	112	217	450	254
Boiling point (1 atm, °C)	−183	444	685	990	962
Electronegativity	3.5	2.5	2.4	2.1	1.9
First ionization energy (kJ/mol)	1314	1000	941	869	812
Atomic radius (Å)	0.73	1.03	1.19	1.42	1.68
Ionic (2−) radius (Å)	1.26	1.70	1.84	2.07	—
Common oxidation states	usually −2	−2, +2, +4, +6	−2, +2, +4, +6	−2, +2, +4, +6	−2, +6

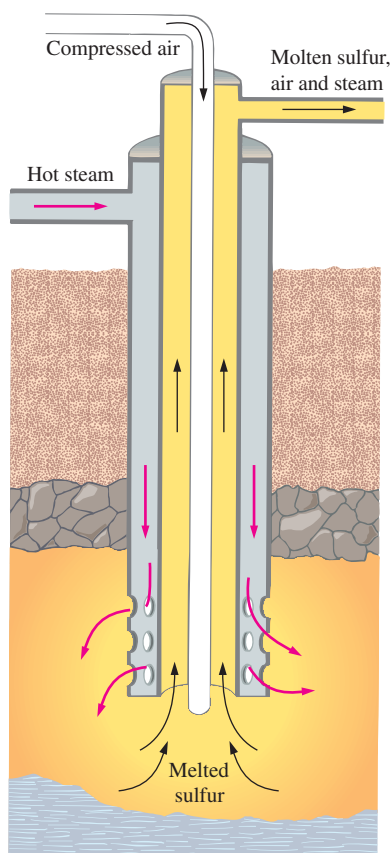


Figure 28-2 The Frasch process for mining sulfur. Three concentric pipes are used. Water at about 170°C and a pressure of 100 lb/in² (7 kg/cm²) is forced down the outermost pipe to melt the sulfur. Hot compressed air is pumped down the innermost pipe. It mixes with the molten sulfur to form a froth, which rises through the third pipe.

Much of the sulfur used in the United States is recovered from sulfur compounds in natural gas and oil. During the oil-refining process, these compounds are reduced to hydrogen sulfide, which is then oxidized to sulfur in the Claus furnace.



Elemental sulfur is mined along the U.S. Gulf Coast by the **Frasch process** (Figure 28-2). Most of it is used in the production of sulfuric acid, H_2SO_4 , the most important of all industrial chemicals. Sulfur is used in the vulcanization of rubber and in the synthesis of many important sulfur-containing organic compounds.

In each of the three physical states, elemental sulfur exists in many forms. The two most stable forms of sulfur, the rhombic (mp 112°C) and monoclinic (mp 119°C) crystalline modifications, consist of different arrangements of S_8 molecules. These are puckered rings containing eight sulfur atoms (see Figure 1-4) and all S—S single bonds. Above 150°C, sulfur becomes increasingly viscous and darkens as the S_8 rings break apart and link into longer chains that become entangled with one another. The viscosity reaches a maximum at 180°C, at which point sulfur is dark brown. Above 180°C, the liquid thins as the chains are broken down into smaller chains. At 444°C, sulfur boils to give a vapor containing S_8 , S_6 , S_4 , and S_2 molecules.

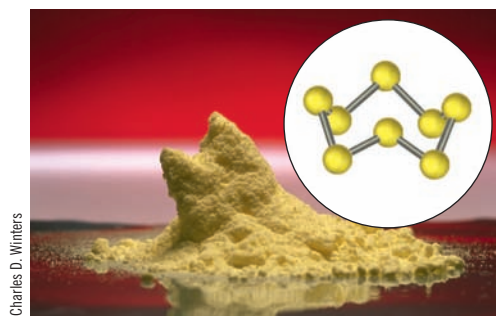
Selenium

Selenium is quite rare (9×10^{-6} % of the earth's crust). It occurs mainly as an impurity in sulfur, sulfide, and sulfate deposits. It is obtained from the flue dusts that result from roasting sulfide ores and from the “anode mud” formed in the electrolytic refining of copper. It is used as a red coloring in glass. The gray crystalline allotropic form of selenium has an electrical conductivity that is very light-sensitive, so it is used in photocopy machines and in solar cells.

Tellurium

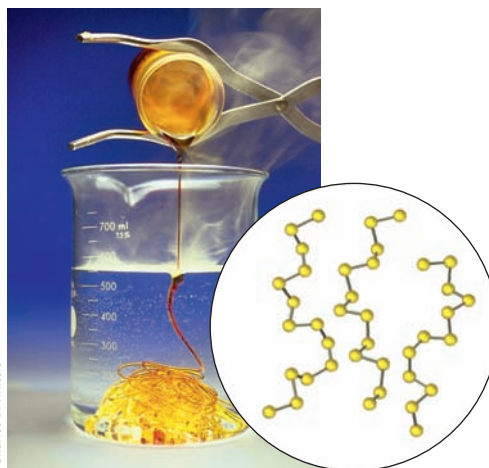
Tellurium is even less abundant (2×10^{-7} % of the earth's crust) than selenium. It occurs mainly in sulfide ores, especially with copper sulfide, and as the tellurides of gold and silver. It, too, is obtained from the “anode mud” from refining of copper. The element forms brass-colored, shiny, hexagonal crystals having low electrical conductivity. It is added to some metals, particularly lead, to increase electrical resistance and improve resistance to heat, corrosion, mechanical shock, and wear.

Unless otherwise noted, all content on this page is © Cengage Learning.



Charles D. Winters

A Yellow crystalline sulfur contains S₈ rings.



Charles D. Winters

B When molten sulfur is heated above 150°C, an amorphous form of sulfur called "plastic sulfur" is formed as the S₈ rings break and the fragments link to form long chains.

Different allotropes of sulfur.

28-9 Reactions of Group 6A Elements

Some reactions of the Group 6A elements are summarized in the following table.

► E represents a Group 6A element.

General Reaction	Remarks
$x\text{E} + y\text{M} \longrightarrow \text{M}_y\text{E}_x$	With many metals
$z\text{E} + \text{M}_x\text{E}_y \longrightarrow \text{M}_x\text{E}_{y+z}$	Especially with S, Se
$\text{E} + \text{H}_2 \longrightarrow \text{H}_2\text{E}$	Decreasingly in the series O ₂ , S, Se, Te
$\text{E} + 3\text{F}_2 \longrightarrow \text{EF}_6$	With S, Se, Te, and excess F ₂
$2\text{E} + \text{Cl}_2 \longrightarrow \text{E}_2\text{Cl}_2$	With S, Se (Te gives TeCl ₂); also with Br ₂
$\text{E}_2\text{Cl}_2 + \text{Cl}_2 \longrightarrow 2\text{ECl}_2$	With S, Se; also with Br ₂
$\text{E} + 2\text{Cl}_2 \longrightarrow \text{ECl}_4$	With S, Se, Te, and excess Cl ₂ ; also with Br ₂
$\text{E} + \text{O}_2 \longrightarrow \text{EO}_2$	With S (with Se, use O ₂ + NO ₂)

28-10 Hydrides of Group 6A Elements

All the Group 6A elements form covalent compounds of the type H₂E (E = O, S, Se, Te, Po) in which the Group 6A element is in the -2 oxidation state. H₂O is a liquid that is essential for animal and plant life. H₂S, H₂Se, and H₂Te are colorless, noxious, poisonous gases. They are even more toxic than HCN. Egg protein contains sulfur, and its decomposition forms H₂S, giving off the odor of rotten eggs. H₂Se and H₂Te smell even worse. Their odors are usually ample warning of the presence of these poisonous gases.

Both the melting point and boiling point of water are very much higher than expected by comparison with those of the heavier hydrides (Figure 13-5). This is a consequence of hydrogen bonding in ice and liquid water (see Section 13-2) caused by the strongly dipolar nature of water molecules. The electronegativity differences between H and the other 6A elements are much smaller than that between H and O, so no H-bonding occurs in H₂S, H₂Se, or H₂Te.

Aqueous solutions of hydrogen sulfide, selenide, and telluride are acidic; acid strength increases as the group is descended: H₂S < H₂Se < H₂Te. The same trend was observed for increasing acidity of the hydrogen halides. The acid ionization constants are

► H₂S is a stronger acid than H₂O. The solubility of H₂S in water is approximately 0.10 mol/L at 25°C.

	H ₂ S	H ₂ Se	H ₂ Te
$\text{H}_2\text{E} \rightleftharpoons \text{H}^+ + \text{HE}^-$	$K_{a1}: 1.0 \times 10^{-7}$	1.9×10^{-4}	2.3×10^{-3}
$\text{HE}^- \rightleftharpoons \text{H}^+ + \text{E}^{2-}$	$K_{a2}: 1.0 \times 10^{-19}$	$\approx 10^{-11}$	$\approx 1.6 \times 10^{-11}$

► Here E represents S, Se, or Te.

28-11 Group 6A Oxides

Although others exist, the most important 6A oxides are the dioxides, which are acid anhydrides of H_2SO_3 , H_2SeO_3 , and H_2TeO_3 ; and the trioxides, which are anhydrides of H_2SO_4 , H_2SeO_4 , and H_6TeO_6 . Let us consider SO_2 and SO_3 as examples.

► +4 Oxidation State

Formula	Name
H_2SO_3	sulfurous acid
H_2SeO_3	selenous acid
H_2TeO_3	tellurous acid

+6 Oxidation State

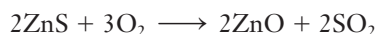
Formula	Name
H_2SO_4	sulfuric acid
H_2SeO_4	selenic acid
H_6TeO_6	telluric acid

► If the SO_2 and SO_3 are allowed to escape into the atmosphere, they cause highly acidic rain.

Sulfur Dioxide, SO_2

Sulfur dioxide is a colorless, poisonous, corrosive gas with a very irritating odor. Even in small quantities, it causes coughing and nose, throat, and lung irritation. It is an angular molecule with trigonal planar electronic geometry, sp^2 hybridization at the S atom, and resonance stabilization.

Sulfur dioxide is produced in reactions such as the combustion of sulfur-containing fossil fuels and the roasting of sulfide ores.



SO_2 is a waste product of these operations. In the past, it was released into the atmosphere along with some SO_3 produced by its reaction with O_2 . A more environmentally friendly practice now is to trap SO_2 and SO_3 and use them to make H_2SO_4 . Some coal contains up to 5% sulfur, so both SO_2 and SO_3 are present in the flue gases when coal is burned. No method has been found to remove all the SO_2 from flue gases of power plants. One way of removing most of the SO_2 involves the injection of limestone, CaCO_3 , into the combustion zone of the furnace. Here CaCO_3 decomposes to lime, CaO . This then combines with SO_2 to form calcium sulfite (CaSO_3), an ionic solid, which is collected and disposed of as solid waste.

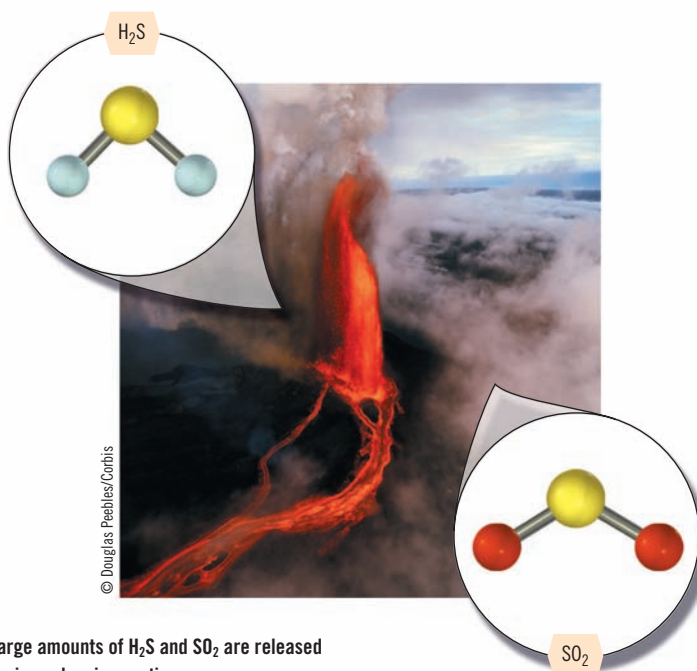


This process is called scrubbing, and a disadvantage of it is the formation of huge quantities of solid waste (CaSO_3 , unreacted CaO , and by-products).

Catalytic oxidation is now used by the smelting industry to convert SO_2 into SO_3 . This is then dissolved in water to make solutions of H_2SO_4 (up to 80% by mass). The gases containing SO_2 are passed through a series of condensers containing catalysts to speed up the reaction. In some cases, the impure H_2SO_4 can be used in other operations in the same plant.



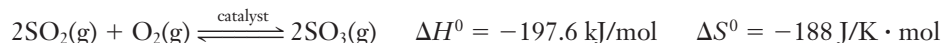
The rose on the right is in an atmosphere of sulfur dioxide, SO_2 . Gaseous SO_2 and aqueous solutions of HSO_3^- and SO_3^{2-} ions are used as bleaching agents. A similar process is used to bleach wood pulp before it is converted to paper.



Large amounts of H_2S and SO_2 are released during volcanic eruptions.

Sulfur Trioxide, SO₃

Sulfur trioxide is a liquid that boils at 44.8°C. It is the anhydride of H₂SO₄. It is formed by the reaction of SO₂ with O₂. The reaction is very exothermic, but ordinarily very slow. It is catalyzed commercially in the **contact process** by spongy Pt, SiO₂, or vanadium(V) oxide, V₂O₅, at high temperatures (400 to 700°C).



The high temperature favors SO₂ and O₂ but allows the reaction to proceed much more rapidly, so it is economically advantageous. The SO₃ is then removed from the gaseous reaction mixture by dissolving it in concentrated H₂SO₄ (95% H₂SO₄ by mass) to produce polysulfuric acids—mainly pyrosulfuric acid, H₂S₂O₇. This is called oleum, or fuming sulfuric acid. The addition of fuming sulfuric acid to water produces commercial H₂SO₄.



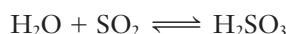
In the presence of certain catalysts, sulfur dioxide in polluted air reacts rapidly with O₂ to form SO₃. Particulate matter, or suspended microparticles, such as NH₄NO₃ and elemental S, act as efficient catalysts.

► The prefix *pyro* means “heat” or “fire.” Pyrosulfuric acid may also be obtained by heating concentrated sulfuric acid, which results in the elimination of one molecule of water from two molecules of sulfuric acid.

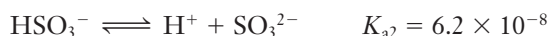
28-12 Oxoacids of Sulfur

Sulfurous Acid, H₂SO₃

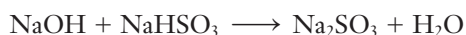
Sulfur dioxide readily dissolves in water to produce solutions of sulfurous acid, H₂SO₃. The acid has not been isolated in anhydrous form and is considered to be the hydrate of SO₂.



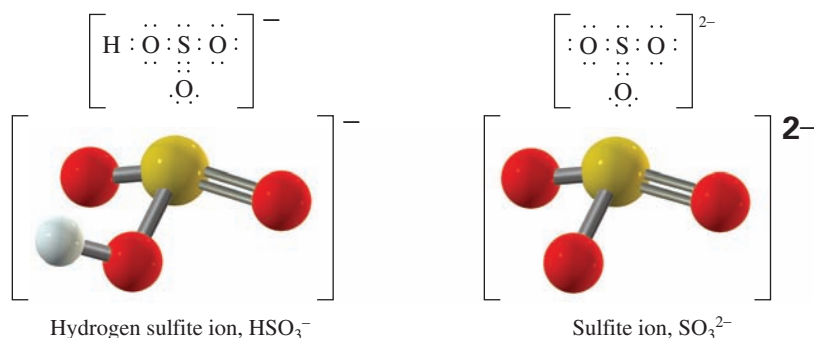
The acid ionizes in two steps in water

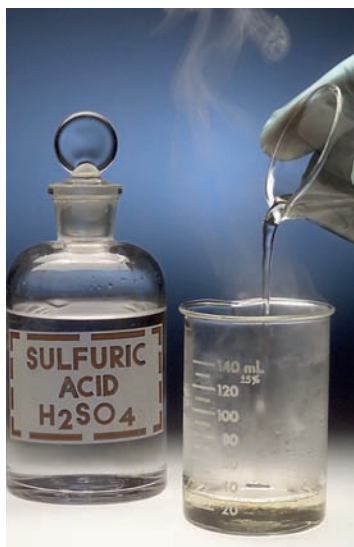


When excess SO₂ is bubbled into aqueous NaOH, sodium hydrogen sulfite, NaHSO₃, is produced. This acidic salt can be neutralized with additional NaOH or Na₂CO₃ to produce sodium sulfite.



The sulfite ion is pyramidal and has tetrahedral electronic geometry, as predicted by the VSEPR theory.





Charles D. Winters

Pouring concentrated H_2SO_4 into an equal volume of H_2O liberates a lot of heat—enough to raise the temperature of the resulting solution by as much as 100°C .

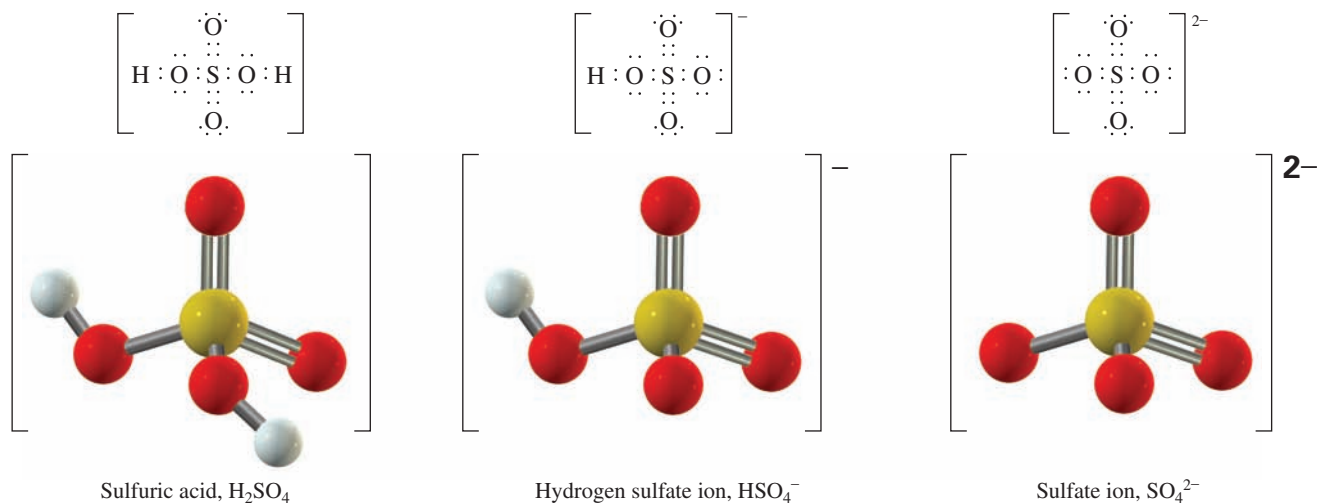
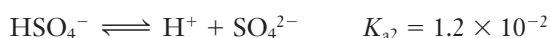
Sulfuric Acid, H_2SO_4

More than 150 million tons of sulfuric acid are produced annually worldwide. The contact process is used for the commercial production of most sulfuric acid. The solution sold commercially as “concentrated sulfuric acid” is 96–98% H_2SO_4 by mass and is about 18 molar H_2SO_4 .

Pure H_2SO_4 is a colorless, oily liquid that freezes at 10.4°C and boils at 290 to 317°C while partially decomposing to SO_3 and water. There is some hydrogen bonding in solid and liquid H_2SO_4 .

Tremendous amounts of heat are evolved when concentrated sulfuric acid is diluted. This illustrates the strong affinity of H_2SO_4 for water. H_2SO_4 is often used as a dehydrating agent. **Dilutions should always be performed by adding the acid to water to avoid spattering the acid.**

Sulfuric acid is a strong acid with respect to the first step of its ionization in water. The second ionization occurs to a lesser extent (see Example 18-18).



Nitrogen and Phosphorus

The Group 5A elements provide a dramatic illustration of the vertical trends in metallic properties. In this family, nitrogen and phosphorus are nonmetals, arsenic is predominantly nonmetallic, antimony is more metallic, and bismuth is definitely metallic. Properties of the Group 5A elements are listed in Table 28-7.

Oxidation states of the 5A elements range from -3 to $+5$. Odd-numbered oxidation states are favored. The 5A elements form very few monatomic ions. Ions with a charge of $3-$ occur for N and P, as in Mg_3N_2 and Ca_3P_2 .

All of the Group 5A elements show the -3 oxidation state in covalent compounds such as NH_3 and PH_3 . The $+5$ oxidation state is found only in covalent compounds such as phosphorus pentafluoride, PF_5 ; nitric acid, HNO_3 ; and phosphoric acid, H_3PO_4 ; and in polyatomic ions such as NO_3^- and PO_4^{3-} . Each Group 5A element exhibits the $+3$ oxidation state in one of its oxides, for instance, N_2O_3 and P_4O_6 . These are acid anhydrides of nitrous acid, HNO_2 , and phosphorous acid, H_3PO_3 ; both are weak acids. No other element exhibits more oxidation states than nitrogen (Table 28-8).

Table 28-7 Properties of the Group 5A Elements

Property	N	P	As	Sb	Bi
Physical state (1 atm, 25°C)	gas	solid	solid	solid	solid
Color	colorless	red, white, black	yellow, gray	yellow, gray	gray
Outermost electrons	$2s^2 2p^3$	$3s^2 3p^3$	$4s^2 4p^3$	$5s^2 5p^3$	$6s^2 6p^3$
Melting point (°C)	−210	44 (white)	813 (gray, 28 atm)*	631 (gray)	271
Boiling point (°C)	−196	280 (white)	sublimes 613	1750	1560
Atomic radius (Å)	0.75	1.10	1.20	1.40	1.50
Electronegativity	3.0	2.1	2.1	1.9	1.8
First ionization energy (kJ/mol)	1402	1012	947	834	703
Oxidation states	−3 to +5	−3 to +5	−3 to +5	−3 to +5	−3 to +5

*Sublimes at lower pressures.

Table 28-8 Oxidation States of Nitrogen with Examples

−3	−2	−1	0	+1	+2	+3	+4	+5
NH ₃ ammonia	N ₂ H ₄ hydrazine	NH ₂ OH hydroxylamine	N ₂ nitrogen	N ₂ O dinitrogen oxide	NO nitrogen oxide	N ₂ O ₃ dinitrogen trioxide	NO ₂ nitrogen dioxide	N ₂ O ₅ dinitrogen pentoxide
NH ₄ ⁺ ammonium ion		NH ₂ Cl chloramine		H ₂ N ₂ O ₂ hyponitrous acid		HNO ₂ nitrous acid	N ₂ O ₄ dinitrogen tetroxide	HNO ₃ nitric acid
NH ₂ [−] amide ion						NO ₂ [−] nitrite ion		NO ₃ [−] nitrate ion

28-13 Occurrence of Nitrogen

Nitrogen, N₂, is a colorless, odorless, tasteless gas that makes up about 75% by mass and 78% by volume of the atmosphere. Nitrogen compounds form only a minor portion of the earth's crust, but all living matter contains nitrogen. The primary natural inorganic deposits of nitrogen are very localized. They consist mostly of KNO₃ and NaNO₃. Most sodium nitrate is mined in Chile.

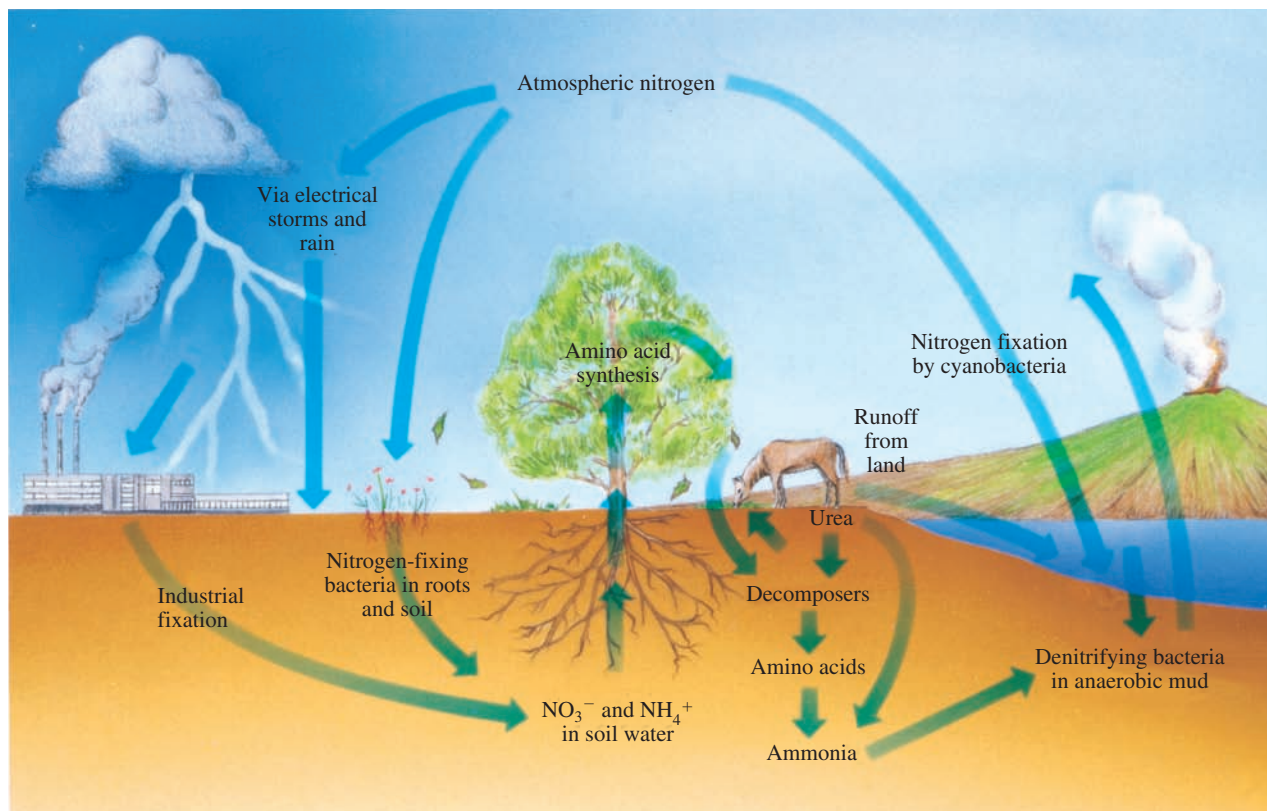
The extreme abundance of N₂ in the atmosphere and the low relative abundance of nitrogen compounds elsewhere are due to the chemical inertness of N₂ molecules. This results from the very high bond energy of the N≡N bond (945 kJ/mol).

Although N₂ molecules are relatively unreactive, nature provides mechanisms by which N atoms are incorporated into proteins, nucleic acids, and other nitrogenous compounds. The **nitrogen cycle** is the complex series of reactions by which nitrogen is slowly but continually recycled in the atmosphere (our nitrogen reservoir), lithosphere (earth), and hydrosphere (water).

When N₂ and O₂ molecules collide near a bolt of lightning, they can absorb enough electrical energy to produce molecules of NO. An NO molecule is quite reactive because it contains one unpaired electron. NO reacts readily with O₂ to form nitrogen dioxide, NO₂. Most NO₂ dissolves in rainwater and falls to the earth's surface. Bacterial enzymes reduce the nitrogen in a series of reactions in which amino acids and proteins are produced. These are then used by plants, eaten by animals, and metabolized. The metabolic products are excreted as nitrogenous compounds such as urea, (NH₂)₂CO, and ammonium salts such as NaNH₄HPO₄. These can also be enzymatically converted to ammonia, NH₃, and amino acids.

► Every protein contains nitrogen in each of its fundamental amino acid units.

► Nitrogen is sold as compressed gas in cylinders. The boiling point of N₂ is −195.8°C (−320°F). N₂ is obtained by fractional distillation of liquid air.



A schematic representation of the nitrogen cycle.



Root nodules on soybeans.

Nitrogen is converted directly into NH_3 in another way. Members of the class of plants called legumes (including soybeans, alfalfa, and clover) have nodules on their roots. Within the nodules live bacteria that produce an enzyme called nitrogenase. These bacteria extract N_2 directly from air trapped in the soil and convert it into NH_3 . The ability of nitrogenase to catalyze this conversion, called *nitrogen fixation*, at ordinary temperatures and pressures with very high efficiency is a marvel to scientists. They must resort to very extreme and costly conditions to produce NH_3 from nitrogen and hydrogen (the Haber process, see Section 17-7).

Ammonia is the source of nitrogen in many fertilizers. Unfortunately, nature does not produce NH_3 and related plant nutrient compounds rapidly enough to provide an adequate food supply for the world's growing population. Commercial synthetic fertilizers have helped to lessen this problem, but at great cost due to the energy that is required to produce them.

28-14 Hydrogen Compounds of Nitrogen

We have already described ammonia and some of its reactions (review Sections 17-7 and 18-4).

Liquid ammonia (bp = -33.4°C) is used as a solvent for some chemical reactions. It is hydrogen bonded, just as H_2O is, but NH_3 is a much more basic solvent. Its weak *autoionization* produces the ammonium ion, NH_4^+ , and the amide ion, NH_2^- . This is similar to H_2O , which ionizes to produce some H_3O^+ and OH^- ions.



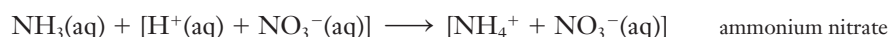
base₂

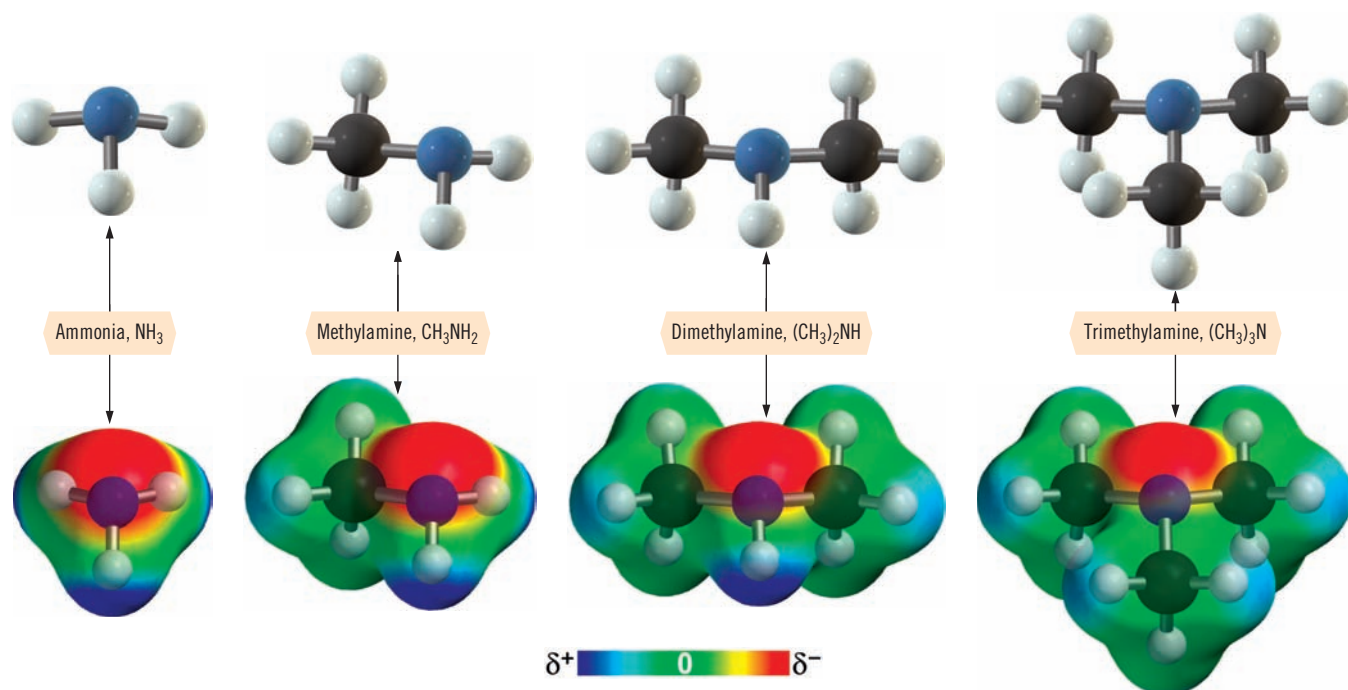
acid₁

acid₂

base₁

Many ammonium salts are known. Most are very soluble in water. They can be prepared by reactions of ammonia with acids. Reaction with nitric acid gives ammonium nitrate.





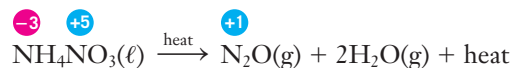
Amines are organic compounds that are structurally related to ammonia. We think of them as being derived from NH_3 by the replacement of one or more hydrogens with organic groups (see Sections 18-4 and 23-12). A series of examples in which the hydrogen atoms are replaced by methyl groups (CH_3) is shown in the figure above. All involve sp^3 -hybridized N. All are weak bases because of the unshared pair of electrons on N.

28-15 Nitrogen Oxides

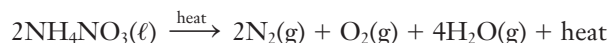
Nitrogen forms several oxides, in which it exhibits positive oxidation states of 1 to 5 (see Table 28-8). All have positive free energies of formation, owing to the high dissociation energy of N_2 and O_2 molecules. All are gases except N_2O_5 , a solid that melts at 30.0°C .

Dinitrogen Oxide (+1 Oxidation State)

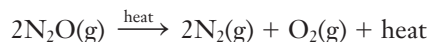
Molten ammonium nitrate undergoes autooxidation–reduction (disproportionation) at 170 to 260°C to produce dinitrogen oxide, also called nitrous oxide.



At higher temperatures, explosions occur, producing N_2 , O_2 , and H_2O .

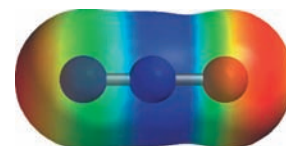


Dinitrogen oxide supports combustion because it produces O_2 when heated.



The molecule is linear but unsymmetrical, with a dipole moment of 0.17 D .

► Some dentists use N_2O for its mild anesthetic properties. It is also known as laughing gas because of its side effects.

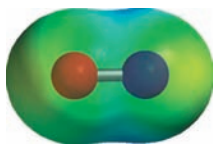


Dinitrogen oxide, or nitrous oxide, N_2O ,
mp = -90.8°C , bp = -88.8°C .

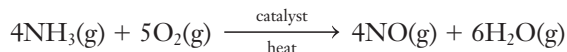
Nitrogen Oxide (+2 Oxidation State)

The first step of the Ostwald process (see Section 28-16) for producing HNO_3 from NH_3 is used for the commercial preparation of nitrogen oxide, NO .

Unless otherwise noted, all content on this page is © Cengage Learning.

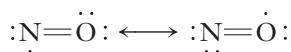


Nitrogen oxide, or nitric oxide, NO, mp = -163.6°C , bp = -151.8°C , bond length (1.15 Å) intermediate between $\text{N} \equiv \text{O}$ (1.06 Å) and $\text{N} = \text{O}$ (1.20 Å).



NO is not produced in large amounts in nature under usual conditions. It is formed by direct reaction of N_2 and O_2 in electrical storms.

NO is a colorless gas that condenses at -152°C to a blue liquid. Gaseous NO is paramagnetic and contains one unpaired electron per molecule.



Its unpaired electron makes nitric oxide very reactive. Molecules that contain unpaired electrons are called *radicals*. NO reacts with O_2 to form NO_2 , a brown, corrosive gas.



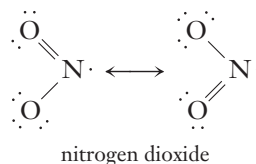
In recent years, researchers have learned that very low concentrations of NO play important roles in a diversity of physiological processes not only in humans, but in a wide variety of animals including barnacles, chickens, trout, and fruit flies. NO has recently been found to be involved in transmission of signals by nerves, blood clotting, local control of blood flow, the immune system's ability to kill tumor cells and bacteria, and possibly even memory.

Nitrogen Dioxide and Dinitrogen Tetroxide (+4 Oxidation State)

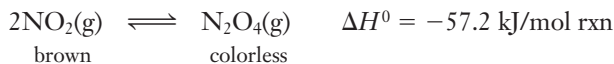
Nitrogen dioxide is formed by reaction of NO with O_2 . It is prepared in the laboratory by heating heavy metal nitrates.



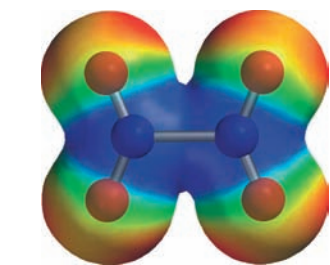
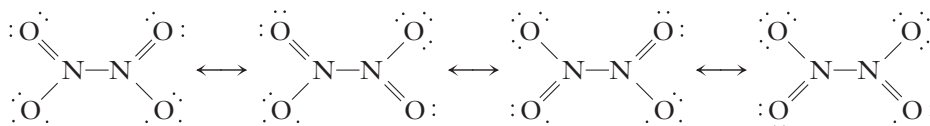
The NO_2 molecule is angular. It is represented by resonance structures.



Because each NO_2 molecule contains one unpaired electron, NO_2 readily dimerizes to form colorless, diamagnetic dinitrogen tetroxide, N_2O_4 , at low temperatures.



The N_2O_4 molecule is also represented by resonance structures.



Dinitrogen tetroxide, N_2O_4 , bp = 21.2°C , no unpaired electrons, N—N bond length 1.64 Å, N—O bond length 1.17 Å, O—N—O bond angle 126° .



CHEMISTRY IN USE

Nitrogen Oxides and Photochemical Smog

Nitrogen oxides are produced in the atmosphere by natural processes. Human activities contribute only about 10% of all the oxides of nitrogen (collectively referred to as NO_x) in the atmosphere, but the human contribution occurs mostly in urban areas, where the oxides may be present in concentrations a hundred times greater than in rural areas.

Just as NO is produced naturally by the reaction of N_2 and O_2 in electrical storms, it is also produced by the same reaction at the high temperatures of internal combustion engines and furnaces.

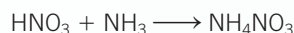


At ordinary temperatures, the reaction does not occur to a significant extent. Because it is endothermic, it is favored by high temperatures. Even in internal combustion engines and furnaces, the equilibrium still lies far to the left, so only small amounts of NO are produced and released into the atmosphere. Even very small concentrations of nitrogen oxides cause serious problems, however.

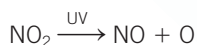
The NO radicals react with O_2 to produce NO_2 radicals. Both NO and NO_2 are quite reactive, and they do considerable damage to plants and animals. NO_2 reacts with H_2O in the air to produce corrosive droplets of HNO_3 (nitric acid) and more NO .



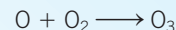
The HNO_3 may be washed out of the air by rainwater (acid rain), or it may react with traces of NH_3 in the air to form solid NH_4NO_3 , a *particulate* pollutant.



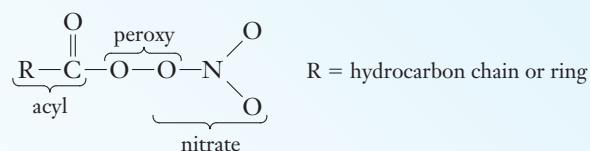
This situation occurs in all urban areas, but the problem is worse in warm, dry climates, which are conducive to light-induced (photochemical) reactions. Here ultraviolet (UV) radiation from the sun produces damaging oxidants. The brownish hazes that often hang over such cities as Los Angeles, Denver, and Mexico City are due to the presence of brown NO_2 . Problems begin in the morning rush hour as NO is exhausted into the air. The NO combines with O_2 to form NO_2 . Then, as the sun rises higher in the sky, NO_2 absorbs UV radiation and breaks down into NO and oxygen radicals.



The extremely reactive O radicals combine with O_2 to produce O_3 (ozone).



Ozone is a powerful oxidizing agent that damages rubber, plastic materials, and all plant and animal life. It also reacts with hydrocarbons from automobile exhaust and evaporated gasoline to form secondary organic pollutants such as aldehydes and ketones (see Section 23-11). The **peroxyacyl nitrates (PANs)**, perhaps the worst of the secondary pollutants, are especially damaging photochemical oxidants that are very irritating to the eyes and throat.



Catalytic converters in automobile exhaust systems reduce emissions of oxides of nitrogen.



Photochemical smog casts a haze over urban or industrial areas; its severity depends on the weather.

► Nitrogen also forms hyponitrous acid, $\text{H}_2\text{N}_2\text{O}_2$, in which N is in the +1 oxidation state, as well as hyponitrite salts such as $\text{Na}_2\text{N}_2\text{O}_2$.

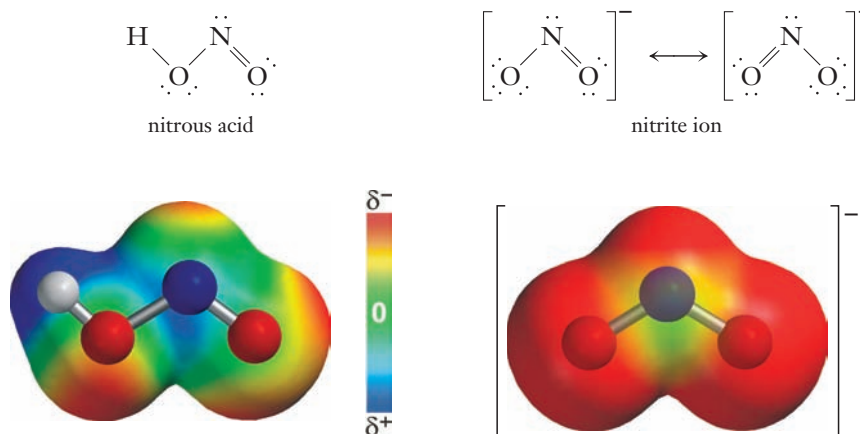
28-16 Some Oxoacids of Nitrogen and Their Salts

The main oxoacids of nitrogen are nitrous acid, HNO_2 , and nitric acid, HNO_3 .

Nitrous Acid (+3 Oxidation State)

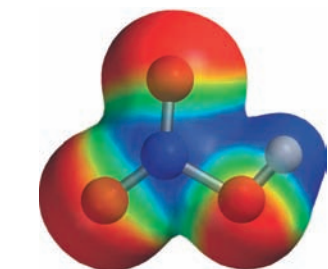
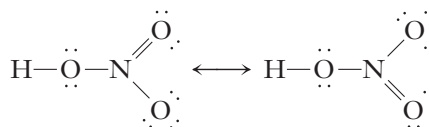
Nitrous acid, HNO_2 , is unstable and cannot be isolated in pure form. It is prepared as a pale blue solution when H_2SO_4 reacts with cold aqueous sodium nitrite. Nitrous acid is a weak acid ($K_a = 4.5 \times 10^{-4}$). It acts as an oxidizing agent toward strong reducing agents and as a reducing agent toward very strong oxidizing agents.

Lewis formulas for nitrous acid and the nitrite ion follow.



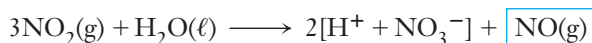
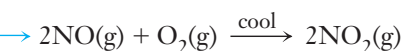
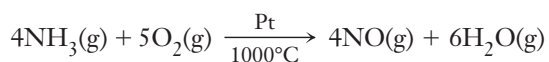
Nitric Acid (+5 Oxidation State)

Pure nitric acid, HNO_3 , is a colorless liquid that boils at 83°C . Light or heat causes it to decompose into NO_2 , O_2 , and H_2O . The presence of the NO_2 in partially decomposed aqueous HNO_3 causes its yellow or brown tinge. The Lewis structure of nitric acid is



Nitric acid, HNO_3 , mp = -42°C ; bp = 83°C ;
bond lengths N—O (terminal) 1.22 Å,
N—OH 1.41 Å.

HNO_3 is commercially prepared by the **Ostwald process**. At high temperatures, NH_3 is catalytically converted to NO , which is cooled and then air-oxidized to NO_2 . Nitrogen dioxide reacts with H_2O to produce HNO_3 and some NO . The NO produced in the third step is then recycled into the second step. More than 18 billion pounds of HNO_3 was produced in the United States in 2010.



recycle



Copper reacts with concentrated nitric acid.
The red-orange gas produced is NO_2 .

Nitric acid is very soluble in water (≈ 16 mol/L). It is a strong acid and a strong oxidizing agent.



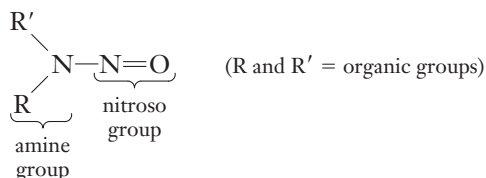
© Cengage Learning/Charles D. Winters

A**B**

Nitric acid, HNO_3 , reacts with protein-containing materials such as this feather, staining them yellow. Perhaps you have spilled nitric acid on your skin and seen it turn yellow.

NaNO_2 and NaNO_3 as Food Additives

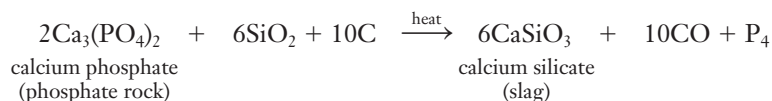
The brown color of “old” meat is the result of oxidation of blood and is objectionable to many consumers. Nitrites and nitrates are added to food to retard this oxidation and also to prevent growth of botulism bacteria. Nitrate ions, NO_3^- , are reduced to NO_2^- ions, which are then converted to NO . This in turn reacts with the brown oxidized form of the heme in blood. This reaction keeps meat red longer. Controversy has arisen, however, concerning the possibility that nitrites combine with amines under the acidic conditions in the stomach to produce carcinogenic *nitrosoamines*.



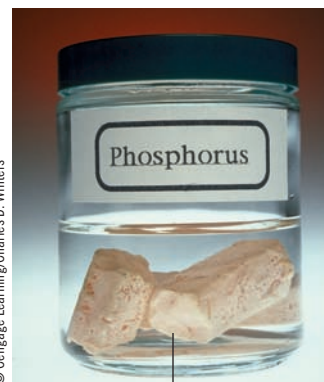
28-17 Phosphorus

Phosphorus is always combined in nature. Phosphorus is present in all living organisms—as organophosphates and in calcium phosphates such as hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, and fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, in bones and teeth. It also occurs in these and related compounds in phosphate minerals, which are mined mostly in Florida and North Africa.

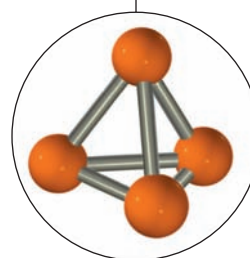
Industrially, the element is obtained from phosphate minerals by heating them at 1200 to 1500°C in an electric arc furnace with sand (SiO_2) and coke.



Vaporized phosphorus is condensed to a white solid (mp = 44.2°C, bp = 280.3°C) under H_2O to prevent oxidation. Even when kept under H_2O , white phosphorus slowly converts to the more stable red phosphorus allotrope (mp = 597°C; sublimes at 431°C). Red phosphorus and tetraphosphorus trisulfide, P_4S_3 , are used in matches. They do not burn



© Cengage Learning/Charles D. Winters



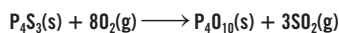
White phosphorus reacts with air, so it is stored under water. It contains tetrahedral P_4 molecules.

Unless otherwise noted, all content on this page is © Cengage Learning.



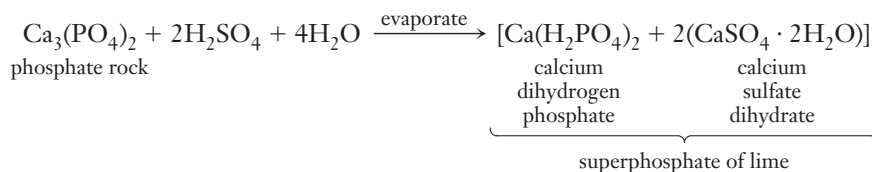
© Cengage Learning/Charles Steele

The tips of “strike anywhere” matches contain tetraphosphorus trisulfide and red phosphorus. Friction converts kinetic energy into heat, which initiates a spontaneous reaction.



spontaneously, yet they ignite easily when heated by friction. Both white and red phosphorus are insoluble in water.

The largest use of phosphorus is in fertilizers. Phosphorus is an essential nutrient, and nature’s phosphorus cycle is very slow due to the low solubility of most natural phosphates. Phosphate fertilizers are therefore essential. To increase the solubility of natural phosphates, they are treated with H_2SO_4 to produce “superphosphate of lime,” a mixture of two salts. This solid is pulverized and applied as a powder.



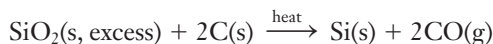
This reaction represents the most popular use of sulfuric acid, the industrial chemical produced in largest quantity in the United States.

Silicon

Silicon is a shiny, blue-gray, high-melting, brittle metalloid. It looks like a metal, but it is chemically more like a nonmetal. It is second only to oxygen in abundance in the earth’s crust, about 87% of which is composed of silica (SiO_2) and its derivatives, the silicate minerals. The crust is 26% Si, compared with 49.5% O. Silicon does not occur in nature as the free element. Pure silicon crystallizes with a diamond-type structure, but the Si atoms are less closely packed than C atoms. Its density is 2.4 g/cm^3 , compared with 3.51 g/cm^3 for diamond.

28-18 Silicon and the Silicates

Elemental silicon is usually prepared by the high-temperature reduction of silica (sand) with coke. Excess SiO_2 prevents the formation of silicon carbide.



Reduction of a mixture of silicon and iron oxides with coke produces an alloy of iron and silicon known as *ferrosilicon*. It is used in the production of acid-resistant steel alloys, such as “duriron,” and in the “deoxidation” of steel. Aluminum alloys for aircraft are strengthened with silicon.

Elemental silicon is used to make silicone polymers. Its semiconducting properties (see Section 13-17) are used in transistors and solar cells.



Courtesy of the U.S. Department of Energy

Pure silicon is used in solar cells to collect energy from the sun.

Unless otherwise noted, all content on this page is © Cengage Learning.

There are several main chemical differences between silicon and carbon. (1) Silicon does not form stable double bonds because Si atoms are much larger than C atoms. As a result, Si—Si bonds are too long to permit effective π -bonding. (2) It does not form very stable Si—Si bonds unless the silicon atoms are bonded to very electronegative elements. (3) It has vacant $3d$ orbitals in its valence shell into which it can accept electrons from donor atoms. This allows Si to exceed an octet electronic configuration and have more than four bonds. The Si—O single bond is one of the strongest of all silicon bonds and accounts for the stability and prominence of silica and the silicates.

Silicon dioxide (silica) exists in two familiar forms in nature: quartz, small chips of which occur in sand; and flint (Latin *silex*), an uncrystallized amorphous type of silica. Silica is properly represented as $(\text{SiO}_2)_n$ because it is a polymeric solid of SiO_4 tetrahedra sharing all oxygens among surrounding tetrahedra (see Figure 13-32c). By comparison, solid carbon dioxide (dry ice) consists of discrete $\text{O}=\text{C}=\text{O}$ molecules, as does gaseous CO_2 .

Some gems and semiprecious stones such as amethyst, opal, agate, and jasper are crystals of quartz with colored impurities.

Most of the crust of the earth is made up of silica and silicates. The natural silicates comprise a large variety of compounds. The structures of all these are based on SiO_4 tetrahedra, with metal ions occupying spaces between the tetrahedra. The extreme stability of the silicates is presumably due to the donation of extra electrons from O into vacant $3d$ orbitals of Si. In many common minerals, called aluminosilicates, Al atoms replace some Si atoms with very little structural change. Because an Al atom has one less positive charge in its nucleus than Si does, it is also necessary to introduce a univalent ion, such as K^+ or Na^+ .

The physical characteristics of the silicates are often suggested by the arrangement of the SiO_4 tetrahedra. A single-chain silicate, diopside $[\text{CaMg}(\text{SiO}_3)_2]_n$, and a double-chain silicate, asbestos $[\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2]_n$, occur as fibrous or needle-like crystals. Talc, $[\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2]_n$, a silicate with a sheet-like structure, is flaky. Micas are sheet-like aluminosilicates with about one of every four Si atoms replaced by Al. Muscovite mica is $[\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2]_n$. Micas occur in thin sheets that are easily peeled away from one another.

The clay minerals are silicates and aluminosilicates with sheet-like structures. They result from the weathering of granite and other rocks. The layers have enormous “inner surfaces” that can absorb large amounts of H_2O . Clay mixtures often occur as minute platelets with a very large total surface area. When wet, the clays are easily shaped. When heated to high temperatures, they lose H_2O ; when fired in a furnace, they become very rigid.

Fused sodium silicate, Na_2SiO_3 , and calcium silicate, CaSiO_3 , are the major components of the glass used in such things as drinking glasses, bottles, and window panes. *Glass* is a hard, brittle material that has no fixed composition or regular structure. Because it has no regular structure, it does not break evenly along crystal planes, but breaks to form rounded surfaces and jagged edges. The basic ingredients are produced by heating a mixture of Na_2CO_3 and CaCO_3 with sand until it melts, at about 700°C .



The resulting “soda–lime” glass is clear and colorless (if all CO_2 bubbles escape and if the amounts of reactants are carefully controlled).

Although Si—O bonds are very strong, Si—F bonds are even stronger. This is why hydrofluoric acid, HF, can attack and dissolve glass, SiO_2 , or any of its variants to form $[\text{SiF}_6]^{2-}$ (aq) ions.



Quartz crystals, SiO_2 .



“Asbestos” refers to a group of impure magnesium silicate minerals. As you can see, this form of asbestos is a fibrous material. When inhaled, these fibers are carcinogenic (they can cause cancer).

KEY TERMS

Amines Organic compounds that are structurally related to ammonia by the replacement of one or more hydrogens.

Chain initiation step The first step in a chain reaction; produces reactive species (such as radicals) that then propagate the reaction.

Chain propagation step An intermediate step in a chain reaction; in such a step one or more reactive species is consumed, and another reactive species is produced.

Chain reaction A reaction in which reactive species, such as radicals, are produced in more than one step. Consists of an initiation step, one or more propagation steps, and one or more termination steps.

Chain termination step The combination of reactive species (such as radicals) that terminates the chain reaction.

Contact process An industrial process by which sulfur trioxide and sulfuric acid are produced from sulfur dioxide.

Frasch process A method by which elemental sulfur is mined or extracted. Sulfur is melted with superheated water (at 170°C under high pressure) and forced to the surface of the earth as a slurry.

Haber process An industrial process for the catalyzed production of ammonia from N_2 and H_2 at high temperature and pressure (see Section 17-7).

Halides Binary compounds of the halogens with less electro-negative elements.

Halogens Group 7A elements; F, Cl, Br, I, and At. The free elements exist as diatomic molecules.

Nitrogen cycle The complex series of reactions by which nitrogen is slowly but continually recycled in the atmosphere, lithosphere, and hydrosphere.

Noble gases Group 8A elements; He, Ne, Ar, Kr, Xe, and Rn.

Ostwald process An industrial process for the production of nitrogen oxide and nitric acid from ammonia and oxygen.

Particulate matter Finely divided solid particles suspended in air.

Peroxyacyl nitrates (PANs) Photochemical oxidants in smog.

Photochemical oxidants Photochemically produced oxidizing agents capable of causing damage to plants and animals.

Photochemical smog A brownish smog occurring in urban areas that receive large amounts of sunlight; caused by photochemical (light-induced) reactions among nitrogen oxides, hydrocarbons, and other components of polluted air that produce photochemical oxidants.

Radical An atom or group of atoms that contains one or more unpaired electrons (usually very reactive species).

EXERCISES

● **Molecular Reasoning** exercises

▲ **More Challenging** exercises

Blue-Numbered exercises are solved in the Student Solutions Manual

The Noble Gases

- (a) Write the Lewis dot formulas for the noble gases. (b) Why are the noble gases so unreactive?
- Why were the noble gases among the last elements to be discovered?
- List some of the uses of the noble gases and reasons for those uses.
- ▲ Arrange the noble gases in order of increasing atomic radii. Explain this trend.
- ▲ Graph the melting points (mp) and boiling points (bp) of the noble gases as a function of their atomic numbers (Z).

	He	Ne	Ar	Kr	Xe	Rn
Z	2	10	18	36	54	86
mp, K	1*	25	84	116	161	202
bp, K	4	27	87	120	165	211
*at 25 atm						

What type of intermolecular force is present in the liquid and solid phases, causing the atoms to attract each other?

- What gave Neil Bartlett the idea that compounds of xenon could be synthesized? Which noble gases are

known to form compounds? With which elements are the noble gas atoms bonded?

- Describe the bonding and geometry in XeF_2 , XeF_4 , and XeF_6 .
- ▲ Xenon(VI) fluoride can be produced by the combination of xenon(IV) fluoride with fluorine. Write a chemical equation for this reaction. What mass of XeF_6 could be produced from 1.85 g of XeF_4 and excess fluorine?

The Halogens

- Write the electron configuration for each halogen atom. Write the Lewis symbol for a halogen atom, X. What is the usual oxidation state of the halogens in binary compounds with metals, semiconducting elements, and most nonmetals?
- Graph the melting points (mp) and boiling points (bp) of hydrogen and the halogens as a function of the number of electrons in the diatomic molecules ($2Z$).

	H_2	F_2	Cl_2	Br_2	I_2	At_2
$2Z$	2	18	34	70	106	170
mp, K	14	53	172	266	387	575
bp, K	20	85	238	332	457	610

● **Molecular Reasoning** exercises

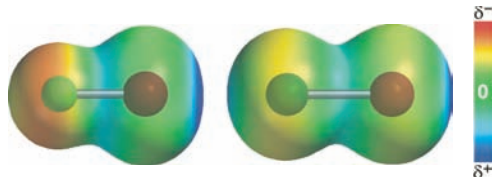
▲ **More Challenging** exercises

Blue-Numbered exercises solved in Student Solutions Manual

Unless otherwise noted, all content on this page is © Cengage Learning.

Compare this graph with the one you produced for Exercise 5. How are they alike? Suggest a reason why they are similar. How are they different?

- What types of intermolecular forces are found in molecular halogens? What is the trend in these forces going down the group from F_2 to I_2 ? Describe the physical state of each molecular halogen at room temperature and pressure.
- List the halogens in order of increasing (a) atomic radii, (b) ionic radii, (c) electronegativities, (d) melting points, (e) boiling points, and (f) standard reduction potentials.
- Write the equations describing the half-reactions and net reaction for the electrolysis of molten KF/HF mixtures. At which electrodes are the products formed? What is the purpose of the HF ?
- Carl O. Christe's preparation of F_2 did not involve direct chemical oxidation. Explain this statement.
- Write equations describing general reactions of the free halogens, X_2 , with (a) Group 1A (alkali) metals, (b) Group 2A (alkaline earth) metals, and (c) Group 3A metals. Represent the metals as M .
- Complete and balance the following equations. If no reaction occurs, write NR.
 (a) $Cl_2(g) + Br^-(aq) \longrightarrow$ (b) $I_2(s) + Cl^-(aq) \longrightarrow$
 (c) $I_2(s) + Br^-(aq) \longrightarrow$ (d) $Br_2(l) + Cl^-(aq) \longrightarrow$
- An aqueous solution contains either $NaBr$ or a mixture of $NaBr$ and NaI . Using only aqueous solutions of I_2 , Br_2 , and Cl_2 and a small amount of CH_2Cl_2 , describe how you might determine what is in the unknown solution.
- Explain the differences between the electrostatic charge potential plots for the interhalogen compounds FCl and $ClBr$.



- Why are the free halogens more soluble in water than most nonpolar molecules? (See Sections 28-6 and 28-7.)
- Distinguish between hydrogen bromide and hydrobromic acid.
- The molecular weights (MW), melting points (mp), and boiling points (bp) for the hydrohalic acids are listed below.

	HF	HCl	HBr	HI
MW	20.01	36.46	80.91	127.9
mp, K	189.6	158.9	186.4	222.4
bp, K	292.7	188.1	206.8	237.8

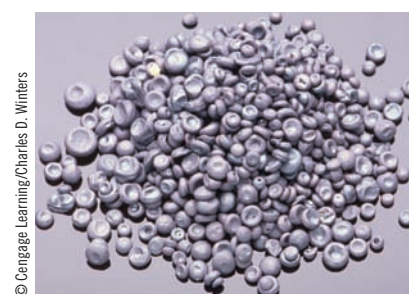
Notice that HCl , HBr , and HI fit a common pattern: the higher the molecular weight, the higher the melting point and the boiling point. Why are both the melting and boiling points of HF higher than what would be predicted from this pattern?

- Describe the effect of hydrofluoric acid on glass.
- What is the acid anhydride of perchloric acid? (See Sections 5-9 and 28-7.)
- Name the following compounds: (a) $KBrO_3$; (b) $KOBr$; (c) $NaClO_4$; (d) $NaBrO_2$; (e) $HOBr$; (f) $HBrO_3$; (g) HIO_3 ; (h) $HClO_4$.

- Write the Lewis formulas and structures of the four ternary acids of chlorine.
- Write equations describing reactions by which the following compounds can be prepared: (a) hypohalous acids of Cl , Br , and I (in solution with hydrohalic acids); (b) hypohalite salts; (c) chlorous acid; (d) perchloric acid.
- Most of the world's supply of bromine is obtained from seawater. The bromide content of seawater is about 1 part in 15,000. Discuss, with the aid of equations, how bromine is produced from seawater.
- Rank the acids in each group from the strongest acid to the weakest. Explain your rankings in terms of molecular properties. (a) $HOCl$, $HOBr$, HOI ; (b) $HOCl$, $HClO_2$, $HClO_3$, $HClO_4$; (c) HOI , $HBrO_3$, $HClO_4$. (See Section 10-7.)

Group 6A Elements

- Write abbreviated electron configurations for atomic oxygen, selenium, and polonium.



Selenium

- Write out the electron configurations of oxide, sulfide, and selenide ions.
- Characterize the Group 6A elements with respect to color and physical state under normal conditions.
- The Group 6A elements, except oxygen, can exhibit oxidation states ranging from -2 to $+6$, but not -3 or $+7$. Why?
- Sulfur, selenium, and tellurium are all capable of forming six-coordinate compounds such as SF_6 . Give two reasons why oxygen cannot be the central atom in such a six-coordinate molecule.
- Write the Lewis formula for (a) H_2S , (b) SF_6 , (c) SF_4 , (d) SO_2 , and (e) SO_3 .
- Draw three-dimensional structures of the molecules listed in Exercise 34 and determine the oxidation number of the central atom(s) of each.
- Write equations for the reactions of (a) S , Se , and Te with excess F_2 ; (b) O_2 , S , Se , and Te with H_2 ; (c) S , Se , and Te with O_2 .
- Write equations for the reactions of (a) S and Te with HNO_3 ; (b) S and Se with excess Cl_2 ; (c) S and Se with Na , Ca , and Al .
- Discuss the acidity of the aqueous Group 6A hydrides, including the relative values of acid ionization constants. What is primarily responsible for the order of increasing acidities in this series?
- Compare the structures of the dioxides of sulfur, selenium, tellurium, and polonium. How do they relate to the metallic or nonmetallic character of these elements? (See Section 5-9.)

40. Write equations for reactions of
 (a) NaOH with sulfuric acid (1:1 mole ratio)
 (b) NaOH with sulfuric acid (2:1 mole ratio)
 (c) NaOH with sulfurous acid (1:1 mole ratio)
 (d) NaOH with sulfurous acid (2:1 mole ratio)
 (e) NaOH with selenic acid, H_2SeO_4 (1:1 mole ratio)
 (f) NaOH with selenic acid (2:1 mole ratio)
 (g) NaOH with tellurium dioxide (1:1 mole ratio)
 (h) NaOH with tellurium dioxide (2:1 mole ratio)
41. ▲ How much sulfur dioxide could be produced from complete combustion of 1.00 ton of coal (carbon) containing 2.85% sulfur?

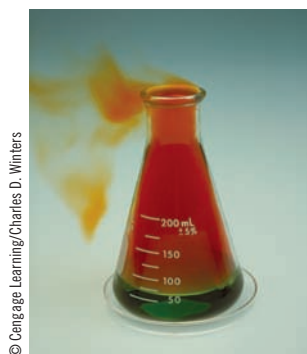


Industrial smokestack

42. What mass of H_2SO_4 could be produced in the following process if 1.25 tons of FeS_2 are used? The *unbalanced* equations for the process are
- $$\text{FeS}_2(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{Fe}_2\text{O}_3(\text{s}) + \text{SO}_2(\text{g})$$
- $$\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{SO}_3(\text{g})$$
- $$\text{SO}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \longrightarrow \text{H}_2\text{S}_2\text{O}_7(\text{l})$$
- $$\text{H}_2\text{S}_2\text{O}_7(\text{l}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{SO}_4(\text{aq})$$
43. Common copper ores in the western United States contain the mineral chalcopyrite, CuFeS_2 . Assuming that a commercially useful ore contains 0.291 mass % Cu and that all the sulfur ultimately appears in the smelter stack gases as SO_2 , calculate the mass of sulfur dioxide generated by the conversion of 1.50 tons of the ore.
44. ▲ A gaseous mixture at some temperature in a 1.00-L vessel originally contained 1.00 mol SO_2 and 5.00 mol O_2 . Once equilibrium conditions were attained, 77.8% of the SO_2 had been converted to SO_3 . What is the value of the equilibrium constant (K_c) for this reaction at this temperature?
52. Determine the oxidation states of nitrogen in the following: (a) N_2 ; (b) N_2O ; (c) N_2O_4 ; (d) HNO_3 ; (e) HNO_2 .
53. ● Draw three-dimensional structures showing all outer-shell electrons, describe molecular and ionic geometries, and indicate hybridization at the central element for the following species: (a) NH_3 ; (b) NH_4^+ ; (c) NH_2^- , amide ion.
54. ● Draw three-dimensional structures showing all outer-shell electrons, describe molecular and ionic geometries, and indicate hybridization at the central element for the following species: (a) NH_2Br , bromamine; (b) HN_3 , hydrazoic acid; (c) N_2O_2 ; (d) $\text{NO}_2^+\text{NO}_3^-$, solid nitronium nitrate; (e) HNO_3 ; (f) NO_2^- .
55. ● Draw three-dimensional structures showing all outer-shell electrons for the following species: (a) P_4 ; (b) P_4O_{10} ; (c) As_4O_6 ; (d) H_3PO_4 ; (e) AsO_4^{3-} .
56. Write formula unit equations for the following: (a) thermal decomposition of potassium azide, KN_3 ; (b) reaction of gaseous ammonia with gaseous HCl ; (c) reaction of aqueous ammonia with aqueous HCl ; (d) thermal decomposition of ammonium nitrate at a temperature above 260°C ; (e) reaction of ammonia with oxygen in the presence of red hot platinum catalyst; (f) thermal decomposition of nitrous oxide (dinitrogen oxide), N_2O ; (g) reaction of NO_2 with water.
57. Write the formula unit equation for the preparation of “superphosphate of lime.”
58. Liquid ammonia, NH_3 , undergoes autoionization, much like water does:
- $$\text{NH}_3(\text{l}) + \text{NH}_3(\text{l}) \longrightarrow \text{NH}_4^+ + \text{NH}_2^- \quad K = 10^{-35}$$
- Name and write the formula for a compound that would be considered an acid in liquid ammonia. Name and write the formula for a compound that would be considered a base in liquid ammonia.
59. Would sodium amide, NaNH_2 , act as an acid or as a base in liquid ammonia? Would ammonium chloride, NH_4Cl , act as an acid or as a base in liquid ammonia? Why?
60. ● Which of the following molecules have a nonzero dipole moment—that is, are polar molecules? (a) NH_3 ; (b) NH_2Cl ; (c) NO_2 ; (d) NH_2OH ; (e) HNO_3
61. Describe with equations the Ostwald process for the production of nitrogen oxide, NO , and nitric acid.
62. ● Why is NO so reactive?
63. ● Write the Lewis formula for NO_2 . Would you predict that NO_2 is very reactive? How about N_2O_4 (dimerized NO_2)?

Nitrogen and Phosphorus

45. ● Characterize each of the Group 5A elements with respect to normal physical state and color.
46. ● Write out complete electron configurations for the atoms of the Group 5A elements; nitride ion, N^{3-} ; and phosphide ion, P^{3-} .
47. ● Compare and contrast the properties of (a) N_2 and P_4 , (b) HNO_3 and H_3PO_4 , (c) N_2O_3 and P_4O_6 .
48. ● Describe the nitrogen cycle.
49. List natural sources of nitrogen and phosphorus and at least two uses for each.
50. Discuss the effects of temperature, pressure, and catalysts on the Haber process for the production of ammonia. (You may wish to consult Section 17-7.)
51. Determine the oxidation states of nitrogen in the following: (a) NO_3^- ; (b) NO ; (c) N_2H_4 ; (d) NH_3 ; (e) NH_2^- .



Nitrogen dioxide

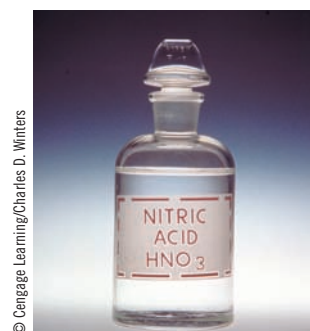
64. At room temperature, a sample of NO_2 gas is brown. Explain why this sample loses its color as it is cooled.
65. Discuss the problem of NO_x emissions with respect to air pollution. Use equations to illustrate the important reactions.
66. What are the acid anhydrides of (a) nitric acid, HNO_3 ; (b) nitrous acid, HNO_2 ; (c) phosphoric acid, H_3PO_4 ; and (d) phosphorous acid, H_3PO_3 ?
67. Calcium phosphate (phosphate rock) is not applied directly as a phosphorus fertilizer. Why?
68. Discuss the use of sodium nitrite as a meat preservative.

Conceptual Exercises

69. Choose the strongest acid from each group:
(a) HClO , HBrO , HIO ; (b) HIO , HIO_3 , HIO_4 ; (c) HIO , HBrO_2 , HBrO_4
70. Write the Lewis structure of a halogen molecule, X_2 . Describe the bonding in the molecule. What is the trend of bond length and strength going down the family from F_2 to I_2 ?
71. Not much is known about astatine because it is very rare, is radioactive, and decays very quickly. Would you predict the chemical and physical properties of astatine to be more like those of a metal or nonmetal? Defend your answer on the basis of astatine's location on the periodic table.
72. Elemental chlorine is obtained by the electrolysis of molten NaCl (Downs cell). Elemental fluorine is obtained by the electrolysis of KHF_2 in a cell made of Monel metal (a stainless steel alloy). Both of these processes are dangerous. Why?
73. Acid rain consists of acids formed by the reaction of acid anhydrides and water. List four acid anhydrides commonly involved in acid rain formation and the sources of each.
74. What ion is always produced when any hydrogen halide $[\text{HX}(\text{g})]$ is dissolved in water?
75. Why are the properties of sulfur, selenium, tellurium, and polonium significantly different from those of oxygen?
76. Why is the molecular structure of sulfur trioxide, SO_3 , different from the ionic structure of the sulfite ion, SO_3^{2-} ?
77. Write a balanced net ionic equation for the disproportionation reaction of (a) hypochlorous acid to chlorine gas and chlorous acid in acidic solution. (b) chlorate ion to perchlorate and chlorite ions.
78. Sulfur deposits are mined by the Frasch process. Explain why free sulfur is not found on the earth's surface.
79. (a) On the basis of electronic structures, explain why most metal halides are ionic. (b) On the basis of your explanation, predict which halide compounds are likely to be covalent.
80. (a) Which of the halogens is the most active chemically and (b) which of the halogens is most likely to be reduced from the free state? (c) Which of the halogens is most likely to act as an oxidizing agent and (d) which of the halogens is least likely to be an effective oxidizing agent?
- (e) Which of the halogens is likely to be a liquid under room conditions? and (f) which of the halogens is most likely to be found in nature as the free element?
81. The nitrogen cycle indicates that electrical storms (lightning) are a source of nitrogen compounds. (a) What is the function of the lightning? (b) What compounds of nitrogen are produced during electrical storms? (c) What is the effect of these compounds on the rainwater?

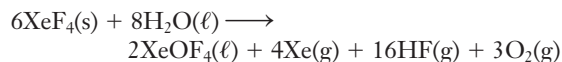
Building Your Knowledge

82. Standard enthalpies of formation are -402 kJ/mol for $\text{XeF}_6(\text{s})$ and -261.5 kJ/mol for $\text{XeF}_4(\text{s})$. Calculate ΔH_{rxn}^0 at 25°C for the preparation of XeF_6 from XeF_4 and $\text{F}_2(\text{g})$.
83. The average atomic mass of N is 14.0067 amu. There are two isotopes that contribute to this average: ^{14}N (14.00307 amu) and ^{15}N (15.00011 amu). Calculate the percentage of ^{15}N atoms in a sample of naturally occurring nitrogen.
84. The $\text{N}-\text{N}$ and the $\text{N}\equiv\text{N}$ bond energies are listed in Tables 15-2 and 15-3. Predict whether four gaseous nitrogen atoms would form two gaseous nitrogen molecules or a gaseous tetrahedral molecule similar to P_4 , basing your prediction on the amount of energy released as the molecules are formed. Repeat the calculations for phosphorus using 201 kJ/mol for $\text{P}-\text{P}$ and 485 kJ/mol for $\text{P}\equiv\text{P}$.
85. Commercial concentrated HNO_3 contains 69.5 mass % HNO_3 and has a density of 1.42 g/mL . What is the molarity of this solution? What volume of the concentrated acid should you use to prepare 5.00 L of dilute HNO_3 solution with a concentration of 6.00 M ?

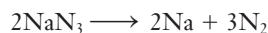


Concentrated nitric acid

86. What is the total mass of silicon in the crust of the earth? Assume that the radius of the earth is 6400 km , the crust is 50 km thick, the density of the crust is 3.5 g/cm^3 , and $25.7 \text{ mass \%}$ of the crust is silicon.
87. How many grams of xenon oxide tetrafluoride, XeOF_4 , and how many liters of HF at STP could be prepared, assuming complete reaction of 15.5 g of xenon tetrafluoride, XeF_4 , with a stoichiometric quantity of water according to the equation below?



88.   Argon crystallizes at -235°C in a face-centered cubic unit cell with $a = 5.43 \text{ \AA}$. Determine the apparent radius of an argon atom in the solid.
89.  A reaction mixture contained 100. g of K_2MnF_6 and 174 g of SbF_5 . Fluorine was produced in 35.3% yield. How many grams of F_2 were produced? What volume is this at STP?
90. Sodium azide, NaN_3 , decomposes explosively to sodium metal and nitrogen gas and is used in automobile airbags.



(a) Draw a Lewis formula for the azide ion, N_3^- , which is isoelectronic with CO_2 . (*Hint*: all three N atoms bear a formal charge.) (b) What is the average oxidation state of nitrogen in the azide anion? (c) Is the nitrogen reduced or oxidized by the decomposition to N_2 gas?

Beyond the Textbook

NOTE: *Whenever the answer to an exercise depends on information obtained from a source other than this textbook, the source must be included as an essential part of the answer.*

91. Open a website containing details about the periodic table and/or history of the elements. Using information found

on the web, answer the following questions. (a) There are eleven nonmetal elements in the earth's atmosphere. Give the name and symbol of each. How many of these elements are diatomic in their natural state? (b) Which element is the second most abundant element in the earth's crust? Is it a metal, metalloid, or nonmetal?

92. Use an internet search engine (such as <http://www.google.com>) to locate information on dietary requirements for selenium. What are the daily minimum and maximum amounts of selenium required? What are some natural sources of selenium in our diets? What are some of the symptoms that might be experienced if one's diet has too little selenium? What if it has too much selenium?
93. Use an internet search engine (such as <http://www.google.com>) to locate information on iodine. Who is given credit for the first isolation of iodine? Why do we use iodized salt? Describe and give an example of naturally iodized salts.
94. The following isotopes of elements discussed in this chapter are important in nuclear magnetic resonance (NMR) spectroscopy: ^{13}C , ^{15}N , ^{19}F , ^{29}Si , ^{31}P , and ^{77}Se . (a) What feature do they possess that is important in NMR spectroscopy? (b) Which of these are most commonly used in NMR spectroscopy and why?

A

Some Mathematical Operations

In chemistry we frequently use very large or very small numbers. Such numbers are conveniently expressed in *scientific*, or *exponential, notation*.

A-1 Scientific Notation

In scientific notation, a number is expressed as the *product of two numbers*. By convention, the first number, called the *digit term*, is between 1 and 10. The second number, called the *exponential term*, is an integer power of 10. Some examples follow.

$$\begin{array}{ll}
 10000 = 1 \times 10^4 & 24327 = 2.4327 \times 10^4 \\
 1000 = 1 \times 10^3 & 7958 = 7.958 \times 10^3 \\
 100 = 1 \times 10^2 & 594 = 5.94 \times 10^2 \\
 10 = 1 \times 10^1 & 98 = 9.8 \times 10^1 \\
 1 = 1 \times 10^0 & \\
 1/10 = 0.1 = 1 \times 10^{-1} & 0.32 = 3.2 \times 10^{-1} \\
 1/100 = 0.01 = 1 \times 10^{-2} & 0.067 = 6.7 \times 10^{-2} \\
 1/1000 = 0.001 = 1 \times 10^{-3} & 0.0049 = 4.9 \times 10^{-3} \\
 1/10000 = 0.0001 = 1 \times 10^{-4} & 0.00017 = 1.7 \times 10^{-4}
 \end{array}$$

► Recall that, by definition, (any base)⁰ = 1.

The exponent of 10 is the number of places the decimal point must be shifted to give the number in long form. A *positive exponent* indicates that the decimal point is *shifted right* that number of places. A *negative exponent* indicates that the decimal point is *shifted left*. When numbers are written in *standard scientific notation*, there is one nonzero digit to the left of the decimal point.

$$\begin{aligned}
 7.3 \times 10^3 &= 73 \times 10^2 &= 730 \times 10^1 &= 7300 \\
 4.36 \times 10^{-2} &= 0.436 \times 10^{-1} &= 0.0436 \\
 0.00862 &= 0.0862 \times 10^{-1} &= 0.862 \times 10^{-2} &= 8.62 \times 10^{-3}
 \end{aligned}$$

In scientific notation the digit term indicates the number of significant figures in the number. The exponential term merely locates the decimal point and does not represent significant figures.

Problem-Solving Tip Know How to Use Your Calculator

Students sometimes make mistakes when they try to enter numbers into their calculators in scientific notation. Suppose you want to enter the number 4.36×10^{-2} . On most calculators, you would

1. Press 4.36
2. Press E, EE, or EXP, which stands for “times ten to the”
3. Press 2 (the magnitude of the exponent) and then $\pm$ or CHS (to change its sign)

► To be sure you know how to use your calculator, you should use it to check the answers to all calculations in this appendix.

The calculator display might show the value as $\boxed{4.36 \quad -02}$ or as $\boxed{0.0436}$. Different calculators show different numbers of digits, which can sometimes be adjusted.

If you wished to enter -4.36×10^2 , you would

1. Press 4.36, then press $\pm$ or CHS to change its sign,
2. Press E, EE, or EXP, and then press 2

The calculator would then show $\boxed{-4.36 \quad 02}$ or $\boxed{-436.0}$.

Caution: Be sure you remember that the E, EE, or EXP button *includes* the “times 10” operation. An error that beginners often make is to enter “ $\times 10$ ” explicitly when trying to enter a number in scientific notation. Suppose you mistakenly enter 3.7×10^2 as follows:

1. Enter 3.7
2. Press $\times$ and then enter 10
3. Press E, EE, or EXP and then enter 2

The calculator then shows the result as 3.7×10^3 or 3700—why? This sequence is processed by the calculator as follows: Step 1 enters the number 3.7; step 2 multiplies by 10, to give 37; step 3 multiplies this by 10^2 , to give 37×10^2 or 3.7×10^3 .

Other common errors include changing the sign of the exponent when the intent was to change the sign of the entire number (e.g., -3.48×10^4 entered as 3.48×10^{-4}).

When in doubt, carry out a trial calculation for which you already know the answer. For instance, multiply 300 by 2 by entering the first value as 3.00×10^2 and then multiplying by 2; you know the answer should be 600, and if you get any other answer, you know you have done something wrong. If you cannot find (or understand) the printed instructions for *your calculator*, your instructor or a classmate might be able to help.

Addition and Subtraction

In addition and subtraction all numbers are converted to the same power of 10, and then the digit terms are added or subtracted.

$$(4.21 \times 10^{-3}) + (1.4 \times 10^{-4}) = (4.21 \times 10^{-3}) + (0.14 \times 10^{-3}) = 4.35 \times 10^{-3}$$

$$(8.97 \times 10^4) - (2.31 \times 10^3) = (8.97 \times 10^4) - (0.231 \times 10^4) = 8.74 \times 10^4$$

Multiplication

The digit terms are multiplied in the usual way, the exponents are added algebraically, and the product is written with one nonzero digit to the left of the decimal.

► Two significant figures in answer.

$$(4.7 \times 10^7)(1.6 \times 10^2) = (4.7)(1.6) \times 10^{7+2} = 7.52 \times 10^9 = 7.5 \times 10^9$$

► Two significant figures in answer.

$$(8.3 \times 10^4)(9.3 \times 10^{-9}) = (8.3)(9.3) \times 10^{4-9} = 77.19 \times 10^{-5} = 7.7 \times 10^{-4}$$

Division

The digit term of the numerator is divided by the digit term of the denominator, the exponents are subtracted algebraically, and the quotient is written with one nonzero digit to the left of the decimal.

► Three significant figures in answer.

$$\frac{8.4 \times 10^7}{2.0 \times 10^3} = \frac{8.4}{2.0} \times 10^{7-3} = 4.2 \times 10^4$$

$$\frac{3.81 \times 10^9}{8.412 \times 10^{-3}} = \frac{3.81}{8.412} \times 10^{9-(-3)} = 0.45292 \times 10^{12} = 4.53 \times 10^{11}$$

Powers of Exponentials

The digit term is raised to the indicated power, and the exponent is multiplied by the number that indicates the power.

$$(1.2 \times 10^3)^2 = (1.2)^2 \times 10^{3 \times 2} = 1.44 \times 10^6 = 1.4 \times 10^6$$

$$(3.0 \times 10^{-3})^4 = (3.0)^4 \times 10^{-3 \times 4} = 81 \times 10^{-12} = 8.1 \times 10^{-11}$$

Electronic Calculators. To square a number: (1) enter the number and (2) touch the (x^2) button.

$$(7.3)^2 = 53.29 = 53 \quad (\text{two sig. figs.})$$

To raise a number y to power x : (1) enter the number; (2) touch the (y^x) button; (3) enter the power; and (4) touch the (=) button.

$$(7.3)^4 = 2839.8241 = 2.8 \times 10^3 \quad (\text{two sig. figs.})$$

$$(7.30 \times 10^2)^5 = 2.0730716 \times 10^{14} = 2.07 \times 10^{14} \quad (\text{three sig. figs.})$$

► These instructions are applicable to most calculators. If your calculator has other notation, consult the instructions for your calculator.

Roots of Exponentials

If a calculator is not used, the exponent must be divisible by the desired root. The root of the digit term is extracted in the usual way, and the exponent is divided by the desired root.

$$\begin{aligned} \sqrt{2.5 \times 10^5} &= \sqrt{2.5 \times 10^4} = \sqrt{25} \times \sqrt{10^4} = 5.0 \times 10^2 \\ \sqrt[3]{2.7 \times 10^{-8}} &= \sqrt[3]{27 \times 10^{-9}} = \sqrt[3]{27} \times \sqrt[3]{10^{-9}} = 3.0 \times 10^{-3} \end{aligned}$$

Electronic Calculators. To extract the square root of a number: (1) enter the number and (2) touch the ($\sqrt{x}$) button.

$$\sqrt{23} = 4.7958315 = 4.8 \quad (\text{two sig. figs.})$$

To extract some other root: (1) enter the number y ; (2) touch the (INV) and then the (y^x) button; (3) enter the root to be extracted, x ; and (4) touch the (=) button.

► On some calculator models, this function is performed by the $\sqrt[y]{y}$ button.

A-2 Logarithms

The logarithm of a number is the power to which a base must be raised to obtain the number. Two types of logarithms are frequently used in chemistry: (1) common logarithms (abbreviated log), whose base is 10, and (2) natural logarithms (abbreviated ln), whose base is $e = 2.71828$. The general properties of logarithms are the same no matter what base is used. Many equations in science were derived by the use of calculus, and these often involve natural (base e) logarithms. The relationship between $\log x$ and $\ln x$ is as follows.

$$\ln x = 2.303 \log x$$

► $\ln 10 = 2.303$

Finding Logarithms. The common logarithm of a number is the power to which 10 must be raised to obtain the number. The number 10 must be raised to the third power to equal 1000. Therefore, the logarithm of 1000 is 3, written $\log 1000 = 3$. Some examples follow.

Number	Exponential Expression	Logarithm
1000	10^3	3
100	10^2	2
10	10^1	1
1	10^0	0
$1/10 = 0.1$	10^{-1}	-1
$1/100 = 0.01$	10^{-2}	-2
$1/1000 = 0.001$	10^{-3}	-3

To obtain the logarithm of a number other than an integral power of 10, you must use either an electronic calculator or a logarithm table. On most calculators, you do this by (1) entering the number and then (2) pressing the (log) button.

$$\begin{aligned} \log 7.39 &= 0.8686444 = 0.869 \\ \log 7.39 \times 10^3 &= 3.8686 = 3.869 \\ \log 7.39 \times 10^{-3} &= -2.1314 = -2.131 \end{aligned}$$

Unless otherwise noted, all content on this page is © Cengage Learning.

The number to the left of the decimal point in a logarithm is called the *characteristic*, and the number to the right of the decimal point is called the *mantissa*. The characteristic only locates the decimal point of the number, so it is usually not included when counting significant figures. The mantissa has as many significant figures as the number whose log was found.

To obtain the natural logarithm of a number on an electronic calculator, (1) enter the number and (2) press the (ln) or (ln x) button.

$$\ln 4.45 = 1.4929041 = 1.493$$

$$\ln 1.27 \times 10^3 = 7.1468 = 7.147$$

► On some calculators, the inverse log is found as follows:

1. enter the value of the log
2. press the (2ndF) (second function) button
3. press (10^x)

On some calculators, the inverse natural logarithm is found as follows:

1. enter the value of the ln
2. press the (2ndF) (second function) button
3. press (e^x)

Finding Antilogarithms. Sometimes we know the logarithm of a number and must find the number. This is called finding the *antilogarithm* (or *inverse logarithm*). To do this on a calculator, (1) enter the value of the log; (2) press the (INV) button; and (3) press the (log) button.

$$\log x = 6.131; \quad \text{so } x = \text{inverse log of } 6.131 = 1.352 \times 10^6$$

$$\log x = -1.562; \quad \text{so } x = \text{inverse log of } -1.562 = 2.74 \times 10^{-2}$$

To find the inverse natural logarithm, (1) enter the value of the ln; (2) press the (INV) button; and (3) press the (ln) or (ln x) button.

$$\ln x = 3.552; \quad \text{so } x = \text{inverse ln of } 3.552 = 3.49 \times 10^1$$

$$\ln x = -1.248; \quad \text{so } x = \text{inverse ln of } -1.248 = 2.87 \times 10^{-1}$$

Calculations Involving Logarithms

Because logarithms are exponents, operations involving them follow the same rules as the use of exponents. The following relationships are useful.

$$\log xy = \log x + \log y \quad \text{or} \quad \ln xy = \ln x + \ln y$$

$$\log \frac{x}{y} = \log x - \log y \quad \text{or} \quad \ln \frac{x}{y} = \ln x - \ln y$$

$$\log x^y = y \log x \quad \text{or} \quad \ln x^y = y \ln x$$

$$\log \sqrt[y]{x} = \log x^{1/y} = \frac{1}{y} \log x \quad \text{or} \quad \ln \sqrt[y]{x} = \ln x^{1/y} = \frac{1}{y} \ln x$$

A-3 Quadratic Equations

Algebraic expressions of the form

$$ax^2 + bx + c = 0$$

are called **quadratic equations**. Each of the constant terms (a , b , and c) may be either positive or negative. All quadratic equations may be solved by the **quadratic formula**.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

To solve the quadratic equation $3x^2 - 4x - 8 = 0$, we use $a = 3$, $b = -4$, and $c = -8$. Substitution of these values into the quadratic formula gives

$$\begin{aligned} x &= \frac{-(-4) \pm \sqrt{(-4)^2 - 4(3)(-8)}}{2(3)} = \frac{4 \pm \sqrt{16 + 96}}{6} \\ &= \frac{4 \pm \sqrt{112}}{6} = \frac{4 \pm 10.6}{6} \end{aligned}$$

The two roots of this quadratic equation are

$$x = 2.4 \quad \text{and} \quad x = -1.1$$

As you construct and solve quadratic equations based on the observed behavior of matter, you must decide which root has physical significance. Examination of the *equation that*

defines x always gives clues about possible values for x . In this way you can tell which is extraneous (has no physical significance). Negative roots are often extraneous.

When you have solved a quadratic equation, you should always check the values you obtained by substituting them into the original equation. In the preceding example we obtained $x = 2.4$ and $x = -1.1$. Substitution of these values into the original quadratic equation, $3x^2 - 4x - 8 = 0$, shows that both roots are correct. Such substitutions often do not give a perfect check because some round-off error has been introduced.

A-4 Significant Figures

There are two kinds of numbers. *Numbers obtained by counting or from definitions are exact numbers.* They are known to be absolutely accurate. For example, the exact number of people in a closed room can be counted, and there is no doubt about the number of people. A dozen eggs is defined as exactly 12 eggs, no more, no fewer (Figure A-1).

Numbers obtained from measurements are not exact. Every measurement involves an estimate. For example, suppose you are asked to measure the length of this page to the nearest 0.1 mm. How do you do it? The smallest divisions (calibration lines) on a meter stick are 1 mm apart (see Figure 1-17). An attempt to measure to 0.1 mm requires estimation. If three different people measure the length of the page to 0.1 mm, will they get the same answer? Probably not. We deal with this problem by using significant figures.

Significant figures are digits believed to be correct by the person who makes a measurement. We assume that the person is competent to use the measuring device. Suppose one measures a distance with a meter stick and reports the distance as 343.5 mm. What does this number mean? In this person's judgment, the distance is greater than 343.4 mm but less than 343.6 mm, and the best estimate is 343.5 mm. The number 343.5 mm contains four significant figures. The last digit, 5, is a *best estimate* and is therefore doubtful, but it is considered to be a significant figure. In reporting numbers obtained from measurements, *we report one estimated digit, and no more.* Because the person making the measurement is not certain that the 5 is correct, it would be meaningless to report the distance as 343.53 mm.

To see more clearly the part significant figures play in reporting the results of measurements, consider Figure A-2a. Graduated cylinders are used to measure volumes of liquids when a high degree of accuracy is not necessary. The calibration lines on a 50-mL graduated cylinder represent 1-mL increments. Estimation of the volume of liquid in a 50-mL cylinder to within 0.2 mL ($\frac{1}{5}$ of one calibration increment) with reasonable certainty is possible. We might measure a volume of liquid in such a cylinder and report the volume as 38.6 mL, that is, to three significant figures.

Burets are used to measure volumes of liquids when higher accuracy is required. The calibration lines on a 50-mL buret represent 0.1-mL increments, allowing us to make estimates to within 0.02 mL ($\frac{1}{5}$ of one calibration increment) with reasonable certainty (Figure A-2b). Experienced individuals estimate volumes in 50-mL burets to 0.01 mL with considerable reproducibility. For example, using a 50-mL buret, we can measure out 38.56 mL (four significant figures) of liquid with reasonable accuracy.

Accuracy refers to how closely a measured value agrees with the correct value. **Precision** refers to how closely individual measurements agree with one another. Ideally, all measurements should be both accurate and precise. Measurements may be quite precise yet quite inaccurate because of some *systematic error*, which is an error repeated in each measurement. (A faulty balance, for example, might produce a systematic error.) Very accurate measurements are seldom imprecise.

Measurements are usually repeated to improve accuracy and precision. Average values obtained from several measurements are usually more reliable than individual measurements. Significant figures indicate how precisely measurements have been made (assuming the person who made the measurements was competent).

Some simple rules govern the use of significant figures.

1. Nonzero digits are always significant.

► An exact number may be thought of as containing an *infinite* number of significant figures.

► There is some uncertainty in all measurements.

► Significant figures indicate the *uncertainty* in measurements.



© Cengage Learning/Charles Steele

© Karen Moskowitz /Stone/Getty Images

A A dozen eggs is exactly 12 eggs.

B A specific swarm of honeybees contains an *exact* number of live bees (though it would be difficult to count them, and any two *swarms* would be unlikely to contain the same exact number of bees).

Figure A-1

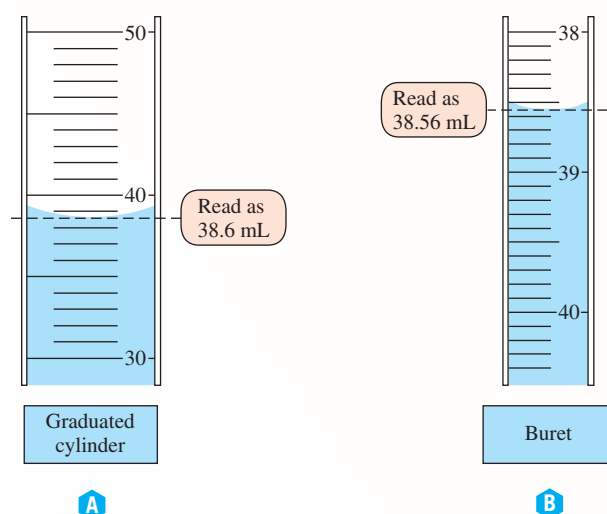


Figure A-2 Measurement of the volume of water using two types of volumetric glassware.

For consistency, we always read the bottom of the meniscus (the curved surface of the water).

(a) A graduated cylinder is used to measure the amount of liquid *contained* in the glassware, so the scale increases from bottom to top. The level in a 50-mL graduated cylinder can usually be estimated to within 0.2 mL. The level here is 38.6 mL (three significant figures). (b) We use a buret to measure the amount of liquid *delivered* from the glassware, by taking the difference between an initial and a final volume reading. The level in a 50-mL buret can be read to within 0.02 mL. The level here is 38.56 mL (four significant figures).

For example, 38.56 mL has four significant figures; 288 g has three significant figures.

2. Zeroes are sometimes significant, and sometimes they are not.

- a.** Zeroes at the *beginning* of a number (used just to position the decimal point) are never significant.

For example, 0.052 g has two significant figures; 0.00364 m has three significant figures. These could also be reported in scientific notation as 5.2×10^{-2} g and 3.64×10^{-3} m, respectively.

- b.** Zeroes *between* nonzero digits are always significant.

For example, 2007 g has four significant figures; 6.08 km has three significant figures.

c. Zeroes at the *end* of a number that contains a decimal point are always significant.

For example, 38.0 cm has three significant figures; 440.0 m has four significant figures. These could also be reported as 3.80×10^1 cm and 4.400×10^2 m, respectively.

d. Zeroes at the *end* of a number that does not contain a decimal point may or may not be significant.

For example, does the quantity 24,300 km represent three, four, or five significant figures? Writing the number in this format gives insufficient information to answer the question. If both of the zeroes are used just to place the decimal point, the number should appear as 2.43×10^4 km (three significant figures). If only one of the zeroes is used to place the decimal point (i.e., the number was measured ± 10), the number is 2.430 ± 10^4 km (four significant figures). If the number is actually known to be $24,300 \pm 1$, it should be written as 2.4300×10^4 km (five significant figures).

► When we wish to specify that all of the zeroes in such a number *are* significant, we may indicate this by placing a decimal point after the number. For instance, 130. grams represents a mass known to *three* significant figures, that is, 130 ± 1 gram.

3. Exact numbers can be considered as having an unlimited number of significant figures. This applies to defined quantities.

For example, in the equivalence 1 yard = 3 feet, the numbers 1 and 3 are exact, and we do not apply the rules of significant figures to them. The equivalence 1 inch = 2.54 centimeters is an exact one.

A calculated number can never be more precise than the numbers used to calculate it. The following rules show how to get the number of significant figures in a calculated number.

4. In addition and subtraction, the last digit retained in the sum or difference is determined by the position of the first doubtful digit.

Example A-1 Significant Figures (Addition and Subtraction)

(a) Add 37.24 mL and 10.3 mL. (b) Subtract 21.2342 g from 27.87 g.

Plan

We first check to see that the quantities to be added or subtracted are expressed in the same units. We carry out the addition or subtraction. Then we follow Rule 4 for significant figures to express the answer to the correct number of significant figures.

Solution

$$\begin{array}{r} 37.24 \text{ mL} \\ + 10.\underline{3} \text{ mL} \\ \hline 47.54 \text{ mL} \end{array}$$

(a) is reported as 47.5 mL (calculator gives 47.54)

$$\begin{array}{r} 27.87 \text{ g} \\ - 21.2342 \text{ g} \\ \hline 6.6358 \text{ g} \end{array}$$

(b) is reported as 6.64 g (calculator gives 6.6358)

STOP & THINK

The doubtful digits are underlined in Example A-1. In addition or subtraction, the last significant digit in the answer is determined by the position of the least doubtful digit. In (a), this is the first digit after the decimal point. In (b), this is the second digit after the decimal point.

5. In multiplication and division, an answer contains no more significant figures than the least number of significant figures used in the operation.

Example A-2 Significant Figures (Multiplication)

What is the area of a rectangle 1.23 cm wide and 12.34 cm long?

Plan

The area of a rectangle is its length times its width. We must first check to see that the width and length are expressed in the same units. (They are, but if they were not, we should first convert one to the units of the other.) Then we multiply the width by the length. We then follow Rule 5 for significant figures to find the correct number of significant figures. The units for the result are equal to the product of the units for the individual terms in the multiplication.

Solution

$$A = \ell \times w = (12.34 \text{ cm})(1.23 \text{ cm}) = 15.2 \text{ cm}^2$$

(calculator result = 15.1782)

Because three is the smallest number of significant figures used, the answer should contain only three significant figures. The number generated by an electronic calculator (15.1782) implies more accuracy than is justified; the result cannot be more accurate than the information that led to it. Calculators have no judgment, so you must exercise yours.

$$\begin{array}{r} \text{▶ } 12.34 \text{ cm} \\ \times 1.23 \text{ cm} \\ \hline 3702 \\ 2468 \\ \underline{1234} \\ 15.17 \end{array} \quad 82 \text{ cm}^2 = 15.2 \text{ cm}^2$$

▶ Rounding to an even number is intended to reduce the accumulation of errors in chains of calculations.

The step-by-step calculation in the margin demonstrates why the area is reported as 15.2 cm^2 rather than 15.1782 cm^2 . The length, 12.34 cm, contains four significant figures, whereas the width, 1.23 cm, contains only three. If we underline each uncertain figure, as well as each figure obtained from an uncertain figure, the step-by-step multiplication gives the result reported in Example A-2. We see that there are only two certain figures (15) in the result. We report the first doubtful figure (.2), but no more. Division is just the reverse of multiplication, and the same rules apply.

In the three simple arithmetic operations we have performed, the number combination generated by an electronic calculator is not the “answer” in a single case! The correct result of each calculation, however, can be obtained by “rounding.” The rules of significant figures tell us where to round.

In rounding off, certain conventions have been adopted. When the number to be dropped is less than 5, the preceding number is left unchanged (e.g., 7.34 rounds to 7.3). When it is more than 5, the preceding number is increased by 1 (e.g., 7.37 rounds to 7.4). When the number to be dropped is 5, the preceding number is set to the nearest even number (e.g., 7.45 rounds to 7.4, and 7.35 rounds to 7.4).

Problem-Solving Tip When Do We Round?

When a calculation involves several steps, we often show the answer to each step to the correct number of significant figures. *But we carry all digits in the calculator to the end of the calculation; then we round the final answer to the appropriate number of significant figures.* When carrying out such a calculation, it is safest to carry extra figures through all steps and then to round the final answer appropriately.

Electronic Configurations of the Atoms of the Elements

APPENDIX

B

Group	1A	2A	3B	4B	5B	6B	7B	8B	1B	2B	3A	4A	5A	6A	7A	8A
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8) (9) (10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	1s															
2	2s															
3	3s															
4	4s															
5	5s															
6	6s															
7	7s															

A periodic table colored to show the kinds of atomic orbitals (subshells) that are being filled in different parts of the periodic table. The atomic orbitals are given below the symbols of blocks of elements. The electronic structures of the A group elements are quite regular and can be predicted from their positions in the periodic table, but there are many exceptions in the *d* and *f* blocks. The populations of subshells are given in the table on pages A-6 and A-7.

Electron Configurations of the Atoms of the Elements

Element	Atomic Number	Populations of Subshells										
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s
H	1	1										
He	2	2										
Li	3	2	1									
Be	4	2	2									
B	5	2	2	1								
C	6	2	2	2								
N	7	2	2	3								
O	8	2	2	4								
F	9	2	2	5								
Ne	10	2	2	6								
Na	11	Neon core			1							
Mg	12				2							
Al	13				2	1						
Si	14				2	2						
P	15				2	3						
S	16				2	4						
Cl	17				2	5						
Ar	18	2	2	6	2	6						
K	19	Argon core						1				
Ca	20							2				
Sc	21						1	2				
Ti	22						2	2				
V	23						3	2				
Cr	24						5	1				
Mn	25						5	2				
Fe	26						6	2				
Co	27						7	2				
Ni	28						8	2				
Cu	29						10	1				
Zn	30						10	2				
Ga	31						10	2	1			
Ge	32						10	2	2			
As	33						10	2	3			
Se	34						10	2	4			
Br	35						10	2	5			
Kr	36	2	2	6	2	6	10	2	6			
Rb	37	Krypton core										1
Sr	38											2
Y	39										1	2
Zr	40										2	2
Nb	41										4	1
Mo	42										5	1
Tc	43										5	2
Ru	44										7	1
Rh	45										8	1
Pd	46										10	
Ag	47										10	1
Cd	48										10	2

Unless otherwise noted, all content on this page is © Cengage Learning.

Electron Configurations of the Atoms of the Elements (continued)

Element	Atomic Number		Populations of Subshells								
			4d	4f	5s	5p	5d	5f	6s	6p	7s
In	49		10		2	1					
Sn	50		10		2	2					
Sb	51		10		2	3					
Te	52		10		2	4					
I	53		10		2	5					
Xe	54		10		2	6					
Cs	55		10		2	6			1		
Ba	56		10		2	6			2		
La	57		10		2	6	1		2		
Ce	58		10	1	2	6	1		2		
Pr	59		10	3	2	6			2		
Nd	60		10	4	2	6			2		
Pm	61		10	5	2	6			2		
Sm	62		10	6	2	6			2		
Eu	63		10	7	2	6			2		
Gd	64		10	7	2	6	1		2		
Tb	65		10	9	2	6			2		
Dy	66		10	10	2	6			2		
Ho	67		10	11	2	6			2		
Er	68		10	12	2	6			2		
Tm	69		10	13	2	6			2		
Yb	70		10	14	2	6			2		
Lu	71		10	14	2	6	1		2		
Hf	72		10	14	2	6	2		2		
Ta	73		10	14	2	6	3		2		
W	74		10	14	2	6	4		2		
Re	75	Krypton core	10	14	2	6	5		2		
Os	76		10	14	2	6	6		2		
Ir	77		10	14	2	6	7		2		
Pt	78		10	14	2	6	9		1		
Au	79		10	14	2	6	10		1		
Hg	80		10	14	2	6	10		2		
Tl	81		10	14	2	6	10		2	1	
Pb	82		10	14	2	6	10		2	2	
Bi	83		10	14	2	6	10		2	3	
Po	84		10	14	2	6	10		2	4	
At	85		10	14	2	6	10		2	5	
Rn	86		10	14	2	6	10		2	6	
Fr	87		10	14	2	6	10		2	6	1
Ra	88		10	14	2	6	10		2	6	2
Ac	89		10	14	2	6	10		2	6	2
Th	90		10	14	2	6	10		2	6	2
Pa	91		10	14	2	6	10	2	2	6	2
U	92		10	14	2	6	10	3	2	6	2
Np	93		10	14	2	6	10	4	2	6	2
Pu	94		10	14	2	6	10	6	2	6	2
Am	95		10	14	2	6	10	7	2	6	2
Cm	96		10	14	2	6	10	7	2	6	2
Bk	97		10	14	2	6	10	9	2	6	2
Cf	98		10	14	2	6	10	10	2	6	2
Es	99		10	14	2	6	10	11	2	6	2
Fm	100		10	14	2	6	10	12	2	6	2
Md	101		10	14	2	6	10	13	2	6	2
No	102		10	14	2	6	10	14	2	6	2
Lr	103		10	14	2	6	10	14	2	6	2
Rf	104		10	14	2	6	10	14	2	6	2
Db	105		10	14	2	6	10	14	2	6	2
Sg	106		10	14	2	6	10	14	2	6	2
Bh	107		10	14	2	6	10	14	2	6	2
Hs	108		10	14	2	6	10	14	2	6	2
Mt	109		10	14	2	6	10	14	2	6	2
Ds	110		10	14	2	6	10	14	2	6	1
Rg	111		10	14	2	6	10	14	2	6	1

Common Units, Equivalences, and Conversion Factors

C-1 Fundamental Units of the SI System

The metric system was implemented by the French National Assembly in 1790 and has been modified many times. The International System of Units, or *le Système International* (SI), represents an extension of the metric system. It was adopted by the eleventh General Conference of Weights and Measures in 1960 and has also been modified since. It is constructed from seven base units, each of which represents a particular physical quantity (Table I).

The first five units listed in Table I are particularly useful in general chemistry. They are defined as follows.

► Alternatives for the standard mass have been proposed.

1. The *meter* is defined as the distance light travels in a vacuum in $1/299,792,458$ second.
2. The *kilogram* represents the mass of a platinum–iridium block kept at the International Bureau of Weights and Measures at Sèvres, France.
3. The *second* was redefined in 1967 as the duration of 9,192,631,770 periods of a certain line in the microwave spectrum of cesium-133.
4. The *kelvin* is $1/273.16$ of the temperature interval between absolute zero and the triple point of water.
5. The *mole* is the amount of substance that contains as many entities as there are atoms in exactly 0.012 kg of carbon-12 (12 g of ^{12}C atoms).

Table I SI Fundamental Units

Physical Quantity	Name of Unit	Symbol
length	meter	m
mass	kilogram	kg
time	second	s
temperature	kelvin	K
amount of substance	mole	mol
electric current	ampere	A
luminous intensity	candela	cd

Prefixes Used with Metric Units and SI Units

Decimal fractions and multiples of metric and SI units are designated by the prefixes listed in Table II. Those most commonly used in general chemistry are underlined.

Table II Traditional Metric and SI Prefixes

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10^{12}	tera	T	10^{-1}	<u>deci</u>	d
10^9	giga	G	10^{-2}	<u>centi</u>	c
10^6	mega	M	10^{-3}	<u>milli</u>	m
10^3	<u>kilo</u>	k	10^{-6}	<u>micro</u>	μ
10^2	hecto	h	10^{-9}	<u>nano</u>	n
10^1	deka	da	10^{-12}	pico	p
			10^{-15}	femto	f
			10^{-18}	atto	a

C-2 Derived SI Units

In the International System of Units all physical quantities are represented by appropriate combinations of the base units listed in Table I. A list of the derived units frequently used in general chemistry is given in Table III.

Table III Derived SI Units

Physical Quantity	Name of Unit	Symbol	Definition
area	square meter	m^2	
volume	cubic meter	m^3	
density	kilogram per cubic meter	kg/m^3	
force	newton	N	$kg \cdot m/s^2$
pressure	pascal	Pa	N/m^2
energy	joule	J	$kg \cdot m^2/s^2$
electric charge	coulomb	C	$A \cdot s$
electric potential difference	volt	V	$J/(A \cdot s)$

Common Units of Mass and Weight

1 pound = 453.59 grams
1 pound = 453.59 grams = 0.45359 kilogram
1 kilogram = 1000 grams = 2.205 pounds
1 gram = 10 decigrams = 100 centigrams = 1000 milligrams
1 gram = 6.022×10^{23} atomic mass units
1 atomic mass unit = 1.6605×10^{-24} gram
1 short ton = 2000 pounds = 907.2 kilograms
1 long ton = 2240 pounds
1 metric tonne = 1000 kilograms = 2205 pounds

Common Units of Length

1 inch = 2.54 centimeters (exactly)
1 mile = 5280 feet = 1.609 kilometers
1 yard = 36 inches = 0.9144 meter
1 meter = 100 centimeters = 39.37 inches = 3.281 feet = 1.094 yards
1 kilometer = 1000 meters = 1094 yards = 0.6215 mile
1 Ångstrom = 1.0×10^{-8} centimeter = 0.10 nanometer = 1.0×10^{-10} meter = 3.937×10^{-9} inch

Common Units of Volume

1 quart = 0.9463 liter 1 liter = 1.056 quarts
1 liter = 1 cubic decimeter = 1000 cubic centimeters = 0.001 cubic meter
1 milliliter = 1 cubic centimeter = 0.001 liter = 1.056×10^{-3} quart
1 cubic foot = 28.316 liters = 29.902 quarts = 7.475 gallons

Common Units of Force* and Pressure

1 atmosphere = 760 millimeters of mercury = 1.01325×10^5 pascals = 1.01325 bar = 14.70 pounds per square inch
1 bar = 10^5 pascals = 0.98692 atm
1 torr = 1 millimeter of mercury
1 pascal = $1 \text{ kg/m} \cdot \text{s}^2 = 1 \text{ N/m}^2$

*Force: 1 newton (N) = $1 \text{ kg} \cdot \text{m/s}^2$, i.e., the force that, when applied for 1 second, gives a 1-kilogram mass a velocity of 1 meter per second.

Common Units of Energy

1 joule = 1×10^7 ergs
1 thermochemical calorie* = 4.184 joules = 4.184×10^7 ergs = 4.129×10^{-2} liter-atmospheres = 2.612×10^{19} electron volts
1 erg = 1×10^{-7} joule = 2.3901×10^{-8} calorie
1 electron volt = 1.6022×10^{-19} joule = 1.6022×10^{-12} erg = 96.487 kJ/mol†
1 liter-atmosphere = 24.217 calories = 101.325 joules = 1.01325×10^9 ergs
1 British thermal unit = 1055.06 joules = 1.05506×10^{10} ergs = 252.2 calories

*The amount of heat required to raise the temperature of one gram of water from 14.5°C to 15.5°C.

†Note that the other units are per particle and must be multiplied by 6.022×10^{23} to be strictly comparable.

D

Physical Constants

Quantity	Symbol	Traditional Units	SI Units
Acceleration of gravity	g	980.665 cm/s	9.80665 m/s
Atomic mass unit ($\frac{1}{12}$ the mass of ^{12}C atom)	amu or u	1.660539×10^{-24} g	1.660539×10^{-27} kg
Avogadro's number	N	$6.02214129 \times 10^{23}$ particles/mol	$6.02214129 \times 10^{23}$ particles/mol
Bohr radius	a_0	0.52918 Å 5.2918×10^{-9} cm	5.2918×10^{-11} m
Boltzmann constant	k	1.3807×10^{-16} erg/K	1.3807×10^{-23} J/K
Charge-to-mass ratio of electron	e/m	1.75882×10^8 coulomb/g	1.75882×10^{11} C/kg
Electronic charge	e	$1.60217656 \times 10^{-19}$ coulomb 4.8033×10^{-10} esu	$1.60217648 \times 10^{-19}$ C
Electron rest mass	m_e	9.1094×10^{-28} g 0.00054858 amu	9.1094×10^{-31} kg
Faraday constant	F	96,485 coulombs/eq 23.06 kcal/volt · eq	96,485 C/mol e^- 96,485 J/V · mol e^-
Gas constant	R	0.08206 $\frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$ 1.987 $\frac{\text{cal}}{\text{mol} \cdot \text{K}}$	8.3145 $\frac{\text{kPa} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}}$ 8.3145 J/mol · K
Molar volume (STP)	V_m	22.414 L/mol	22.414×10^{-3} m ³ /mol 22.414 dm ³ /mol
Neutron rest mass	m_n	1.67493×10^{-24} g 1.008665 amu	1.67493×10^{-27} kg
Planck constant	h	$6.62606957 \times 10^{-27}$ erg · s	$6.62606896 \times 10^{-34}$ J · s
Proton rest mass	m_p	1.6726×10^{-24} g 1.007277 amu	1.6726×10^{-27} kg
Rydberg constant	R_∞	3.2898×10^{15} cycles/s 2.17987×10^{-11} erg	1.09737×10^7 m ⁻¹ 2.17987×10^{-18} J
Speed of light (in a vacuum)	c	$2.99792458 \times 10^{10}$ cm/s (186,281 miles/second)	2.99792458×10^8 m/s

$$\pi = 3.1416 \quad 2.303 R = 4.576 \text{ cal/mol} \cdot \text{K} = 19.15 \text{ J/mol} \cdot \text{K}$$

$$e = 2.71828 \quad 2.303 RT (\text{at } 25^\circ\text{C}) = 1364 \text{ cal/mol} = 5709 \text{ J/mol}$$

$$\ln X = 2.303 \log X$$

Some Physical Constants for a Few Common Substances

Specific Heats and Heat Capacities for Some Common Substances

Substance	Specific Heat (J/g · °C)	Molar Heat Capacity (J/mol · °C)
Al(s)	0.900	24.3
Ca(s)	0.653	26.2
Cu(s)	0.385	24.5
Fe(s)	0.444	24.8
Hg(l)	0.138	27.7
H ₂ O(s), ice	2.09	37.7
H ₂ O(l), water	4.18	75.3
H ₂ O(g), steam	2.03	36.4
C ₆ H ₆ (l), benzene	1.74	136
C ₆ H ₆ (g), benzene	1.04	81.6
C ₂ H ₅ OH(l), ethanol	2.46	113
C ₂ H ₅ OH(g), ethanol	0.954	420
(C ₂ H ₅) ₂ O(l), diethyl ether	3.74	172
(C ₂ H ₅) ₂ O(g), diethyl ether	2.35	108

Heats of Transformation and Transformation Temperatures of Several Substances

Substance	mp (°C)	Heat of Fusion (J/g)	ΔH_{fus} (kJ/mol)	bp (°C)	Heat of Vaporization (J/g)	ΔH_{vap} (kJ/mol)
Al	658	395	10.6	2467	10520	284
Ca	851	233	9.33	1487	4030	162
Cu	1083	205	13.0	2595	4790	305
H ₂ O	0.0	334	6.02	100	2260	40.7
Fe	1530	267	14.9	2735	6340	354
Hg	−39	11	23.3	357	292	58.6
CH ₄	−182	58.6	0.92	−164	—	—
C ₂ H ₅ OH	−117	109	5.02	78.3	855	39.3
C ₆ H ₆	5.48	127	9.92	80.1	395	30.8
(C ₂ H ₅) ₂ O	−116	97.9	7.66	35	351	26.0

Vapor Pressure of Water at Various Temperatures

Temperature (°C)	Vapor Pressure (torr)	Temperature (°C)	Vapor Pressure (torr)	Temperature (°C)	Vapor Pressure (torr)	Temperature (°C)	Vapor Pressure (torr)
−10	2.1	21	18.7	51	97.2	81	369.7
−9	2.3	22	19.8	52	102.1	82	384.9
−8	2.5	23	21.1	53	107.2	83	400.6
−7	2.7	24	22.4	54	112.5	84	416.8
−6	2.9	25	23.8	55	118.0	85	433.6
−5	3.2	26	25.2	56	123.8	86	450.9
−4	3.4	27	26.7	57	129.8	87	468.7
−3	3.7	28	28.3	58	136.1	88	487.1
−2	4.0	29	30.0	59	142.6	89	506.1
−1	4.3	30	31.8	60	149.4	90	525.8
0	4.6	31	33.7	61	156.4	91	546.1
1	4.9	32	35.7	62	163.8	92	567.0
2	5.3	33	37.7	63	171.4	93	588.6
3	5.7	34	39.9	64	179.3	94	610.9
4	6.1	35	42.2	65	187.5	95	633.9
5	6.5	36	44.6	66	196.1	96	657.6
6	7.0	37	47.1	67	205.0	97	682.1
7	7.5	38	49.7	68	214.2	98	707.3
8	8.0	39	52.4	69	223.7	99	733.2
9	8.6	40	55.3	70	233.7	100	760.0
10	9.2	41	58.3	71	243.9	101	787.6
11	9.8	42	61.5	72	254.6	102	815.9
12	10.5	43	64.8	73	265.7	103	845.1
13	11.2	44	68.3	74	277.2	104	875.1
14	12.0	45	71.9	75	289.1	105	906.1
15	12.8	46	75.7	76	301.4	106	937.9
16	13.6	47	79.6	77	314.1	107	970.6
17	14.5	48	83.7	78	327.3	108	1004.4
18	15.5	49	88.0	79	341.0	109	1038.9
19	16.5	50	92.5	80	355.1	110	1074.6
20	17.5						

Ionization Constants for Weak Acids at 25°C

Acid	Formula and Ionization Equation			K_a	pK_a
Acetic	CH_3COOH	$\rightleftharpoons$	$\text{H}^+ + \text{CH}_3\text{COO}^-$	1.8×10^{-5}	4.74
Arsenic	H_3AsO_4	$\rightleftharpoons$	$\text{H}^+ + \text{H}_2\text{AsO}_4^-$	$2.5 \times 10^{-4} = K_{a1}$	3.60
	H_2AsO_4^-	$\rightleftharpoons$	$\text{H}^+ + \text{HAsO}_4^{2-}$	$5.6 \times 10^{-8} = K_{a2}$	7.25
	HAsO_4^{2-}	$\rightleftharpoons$	$\text{H}^+ + \text{AsO}_4^{3-}$	$3.0 \times 10^{-13} = K_{a3}$	12.52
Arsenous	H_3AsO_3	$\rightleftharpoons$	$\text{H}^+ + \text{H}_2\text{AsO}_3^-$	$6.0 \times 10^{-10} = K_{a1}$	9.22
	H_2AsO_3^-	$\rightleftharpoons$	$\text{H}^+ + \text{HAsO}_3^{2-}$	$3.0 \times 10^{-14} = K_{a2}$	13.52
Benzoic	$\text{C}_6\text{H}_5\text{COOH}$	$\rightleftharpoons$	$\text{H}^+ + \text{C}_6\text{H}_5\text{COO}^-$	6.3×10^{-5}	4.20
Boric*	B(OH)_3	$\rightleftharpoons$	$\text{H}^+ + \text{BO(OH)}_2^-$	$7.3 \times 10^{-10} = K_{a1}$	9.14
	BO(OH)_2^-	$\rightleftharpoons$	$\text{H}^+ + \text{BO}_2(\text{OH})^{2-}$	$1.8 \times 10^{-13} = K_{a2}$	12.74
	$\text{BO}_2(\text{OH})^{2-}$	$\rightleftharpoons$	$\text{H}^+ + \text{BO}_3^{3-}$	$1.6 \times 10^{-14} = K_{a3}$	13.80
Carbonic	H_2CO_3	$\rightleftharpoons$	$\text{H}^+ + \text{HCO}_3^-$	$4.2 \times 10^{-7} = K_{a1}$	6.38
	HCO_3^-	$\rightleftharpoons$	$\text{H}^+ + \text{CO}_3^{2-}$	$4.8 \times 10^{-11} = K_{a2}$	10.32
Citric	$\text{C}_3\text{H}_5\text{O(COOH)}_3$	$\rightleftharpoons$	$\text{H}^+ + \text{C}_4\text{H}_5\text{O}_3(\text{COOH})_2^-$	$7.4 \times 10^{-3} = K_{a1}$	2.13
	$\text{C}_4\text{H}_5\text{O}_3(\text{COOH})_2^-$	$\rightleftharpoons$	$\text{H}^+ + \text{C}_5\text{H}_5\text{O}_5\text{COOH}^{2-}$	$1.7 \times 10^{-5} = K_{a2}$	4.77
	$\text{C}_5\text{H}_5\text{O}_5\text{COOH}^{2-}$	$\rightleftharpoons$	$\text{H}^+ + \text{C}_6\text{H}_5\text{O}_7^{3-}$	$7.4 \times 10^{-7} = K_{a3}$	6.13
Cyanic	HOCN	$\rightleftharpoons$	$\text{H}^+ + \text{OCN}^-$	3.5×10^{-4}	3.46
Formic	HCOOH	$\rightleftharpoons$	$\text{H}^+ + \text{HCOO}^-$	1.8×10^{-4}	3.74
Hydrazoic	HN_3	$\rightleftharpoons$	$\text{H}^+ + \text{N}_3^-$	1.9×10^{-5}	4.72
Hydrocyanic	HCN	$\rightleftharpoons$	$\text{H}^+ + \text{CN}^-$	4.0×10^{-10}	9.40
Hydrofluoric	HF	$\rightleftharpoons$	$\text{H}^+ + \text{F}^-$	7.2×10^{-4}	3.14
Hydrogen peroxide	H_2O_2	$\rightleftharpoons$	$\text{H}^+ + \text{HO}_2^-$	2.4×10^{-12}	11.62
Hydrosulfuric	H_2S	$\rightleftharpoons$	$\text{H}^+ + \text{HS}^-$	$1.0 \times 10^{-7} = K_{a1}$	7.00
	HS^-	$\rightleftharpoons$	$\text{H}^+ + \text{S}^{2-}$	$1.0 \times 10^{-19} = K_{a2}$	19.00
Hypobromous	HOBr	$\rightleftharpoons$	$\text{H}^+ + \text{OBr}^-$	2.5×10^{-9}	8.60

Acid	Formula and Ionization Equation			K_a	pK_a
Hypochlorous	HOCl	$\rightleftharpoons$	$H^+ + OCl^-$	3.5×10^{-8}	7.46
Hypoiodous	HOI	$\rightleftharpoons$	$H^+ + OI^-$	2.3×10^{-11}	10.64
Nitrous	HNO ₂	$\rightleftharpoons$	$H^+ + NO_2^-$	4.5×10^{-4}	3.35
Oxalic	(COOH) ₂	$\rightleftharpoons$	$H^+ + COOCOOH^-$	$5.9 \times 10^{-2} = K_{a1}$	1.23
	COOCOOH ⁻	$\rightleftharpoons$	$H^+ + (COO)_2^{2-}$	$6.4 \times 10^{-5} = K_{a2}$	4.19
Phenol	HC ₆ H ₅ O	$\rightleftharpoons$	$H^+ + C_6H_5O^-$	1.3×10^{-10}	9.89
Phosphoric	H ₃ PO ₄	$\rightleftharpoons$	$H^+ + H_2PO_4^-$	$7.5 \times 10^{-3} = K_{a1}$	2.12
	H ₂ PO ₄ ⁻	$\rightleftharpoons$	$H^+ + HPO_4^{2-}$	$6.2 \times 10^{-8} = K_{a2}$	7.21
	HPO ₄ ²⁻	$\rightleftharpoons$	$H^+ + PO_4^{3-}$	$3.6 \times 10^{-13} = K_{a3}$	12.44
Phosphorous	H ₃ PO ₃	$\rightleftharpoons$	$H^+ + H_2PO_3^-$	$1.6 \times 10^{-2} = K_{a1}$	1.80
	H ₂ PO ₃ ⁻	$\rightleftharpoons$	$H^+ + HPO_3^{2-}$	$7.0 \times 10^{-7} = K_{a2}$	6.15
Selenic	H ₂ SeO ₄	$\rightleftharpoons$	$H^+ + HSeO_4^-$	Very large = K_{a1}	
	HSeO ₄ ⁻	$\rightleftharpoons$	$H^+ + SeO_4^{2-}$	$1.2 \times 10^{-2} = K_{a2}$	1.92
Selenous	H ₂ SeO ₃	$\rightleftharpoons$	$H^+ + HSeO_3^-$	$2.7 \times 10^{-3} = K_{a1}$	2.57
	HSeO ₃ ⁻	$\rightleftharpoons$	$H^+ + SeO_3^{2-}$	$2.5 \times 10^{-7} = K_{a2}$	6.60
Sulfuric	H ₂ SO ₄	$\rightleftharpoons$	$H^+ + HSO_4^-$	Very large = K_{a1}	
	HSO ₄ ⁻	$\rightleftharpoons$	$H^+ + SO_4^{2-}$	$1.2 \times 10^{-2} = K_{a2}$	1.92
Sulfurous	H ₂ SO ₃	$\rightleftharpoons$	$H^+ + HSO_3^-$	$1.2 \times 10^{-2} = K_{a1}$	1.92
	HSO ₃ ⁻	$\rightleftharpoons$	$H^+ + SO_3^{2-}$	$6.2 \times 10^{-8} = K_{a2}$	7.21
Tellurous	H ₂ TeO ₃	$\rightleftharpoons$	$H^+ + HTeO_3^-$	$2 \times 10^{-3} = K_{a1}$	2.70
	HTeO ₃ ⁻	$\rightleftharpoons$	$H^+ + TeO_3^{2-}$	$1 \times 10^{-8} = K_{a2}$	8.00

*Boric acid acts as a Lewis acid in aqueous solution.

Ionization Constants for Weak Bases at 25°C

Base	Formula and Ionization Equation				K_b	pK_b
Ammonia	NH_3	$+ \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+$	$+ \text{OH}^-$		1.8×10^{-5}	7.74
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	$+ \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+$	$+ \text{OH}^-$		4.2×10^{-10}	9.38
Dimethylamine	$(\text{CH}_3)_2\text{NH}$	$+ \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_2\text{NH}_2^+$	$+ \text{OH}^-$		7.4×10^{-4}	3.13
Ethylenediamine	$(\text{CH}_2)_2(\text{NH}_2)_2$	$+ \text{H}_2\text{O} \rightleftharpoons (\text{CH}_2)_2(\text{NH}_2)_2\text{H}^+$	$+ \text{OH}^-$		$8.5 \times 10^{-5} = K_{b1}$	4.07
	$(\text{CH}_2)_2(\text{NH}_2)_2\text{H}^+$	$+ \text{H}_2\text{O} \rightleftharpoons (\text{CH}_2)_2(\text{NH}_2)_2\text{H}_2^{2+}$	$+ \text{OH}^-$		$2.7 \times 10^{-8} = K_{b2}$	7.57
Hydrazine	N_2H_4	$+ \text{H}_2\text{O} \rightleftharpoons \text{N}_2\text{H}_5^+$	$+ \text{OH}^-$		$8.5 \times 10^{-7} = K_{b1}$	6.07
	N_2H_5^+	$+ \text{H}_2\text{O} \rightleftharpoons \text{N}_2\text{H}_6^{2+}$	$+ \text{OH}^-$		$8.9 \times 10^{-16} = K_{b2}$	15.05
Hydroxylamine	NH_2OH	$+ \text{H}_2\text{O} \rightleftharpoons \text{NH}_3\text{OH}^+$	$+ \text{OH}^-$		6.6×10^{-9}	8.18
Methylamine	CH_3NH_2	$+ \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+$	$+ \text{OH}^-$		5.0×10^{-4}	3.30
Pyridine	$\text{C}_5\text{H}_5\text{N}$	$+ \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+$	$+ \text{OH}^-$		1.5×10^{-9}	8.82
Trimethylamine	$(\text{CH}_3)_3\text{N}$	$+ \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3)_3\text{NH}^+$	$+ \text{OH}^-$		7.4×10^{-5}	4.13

Solubility Product Constants for Some Inorganic Compounds at 25°C

Substance	K_{sp}	Substance	K_{sp}
Aluminum compounds		Chromium compounds	
AlAsO ₄	1.6×10^{-16}	CrAsO ₄	7.8×10^{-21}
Al(OH) ₃	1.9×10^{-33}	Cr(OH) ₃	6.7×10^{-31}
AlPO ₄	1.3×10^{-20}	CrPO ₄	2.4×10^{-23}
Antimony compounds		Cobalt compounds	
Sb ₂ S ₃	1.6×10^{-93}	Co ₃ (AsO ₄) ₂	7.6×10^{-29}
Barium compounds		CoCO ₃	8.0×10^{-13}
Ba ₃ (AsO ₄) ₂	1.1×10^{-13}	Co(OH) ₂	2.5×10^{-16}
BaCO ₃	8.1×10^{-9}	CoS (α)	5.9×10^{-21}
BaC ₂ O ₄ · 2H ₂ O*	1.1×10^{-7}	CoS (β)	8.7×10^{-23}
BaCrO ₄	2.0×10^{-10}	Co(OH) ₃	4.0×10^{-45}
BaF ₂	1.7×10^{-6}	Co ₂ S ₃	2.6×10^{-124}
Ba(OH) ₂ · 8H ₂ O*	5.0×10^{-3}	Copper compounds	
Ba ₃ (PO ₄) ₂	1.3×10^{-29}	CuBr	5.3×10^{-9}
BaSeO ₄	2.8×10^{-11}	CuCl	1.9×10^{-7}
BaSO ₃	8.0×10^{-7}	CuCN	3.2×10^{-20}
BaSO ₄	1.1×10^{-10}	Cu ₂ O (Cu ⁺ + OH ⁻) [†]	1.0×10^{-14}
Bismuth compounds		CuI	5.1×10^{-12}
BiOCl	7.0×10^{-9}	Cu ₂ S	1.6×10^{-48}
BiO(OH)	1.0×10^{-12}	CuSCN	1.6×10^{-11}
Bi(OH) ₃	3.2×10^{-40}	Cu ₃ (AsO ₄) ₂	7.6×10^{-36}
BiI ₃	8.1×10^{-19}	CuCO ₃	2.5×10^{-10}
BiPO ₄	1.3×10^{-23}	Cu ₂ [Fe(CN) ₆]	1.3×10^{-16}
Bi ₂ S ₃	1.6×10^{-72}	Cu(OH) ₂	1.6×10^{-19}
Cadmium compounds		CuS	8.7×10^{-36}
Cd ₃ (AsO ₄) ₂	2.2×10^{-32}	Gold compounds	
CdCO ₃	2.5×10^{-14}	AuBr	5.0×10^{-17}
Cd(CN) ₂	1.0×10^{-8}	AuCl	2.0×10^{-13}
Cd ₂ [Fe(CN) ₆]	3.2×10^{-17}	AuI	1.6×10^{-23}
Cd(OH) ₂	1.2×10^{-14}	AuBr ₃	4.0×10^{-36}
CdS	3.6×10^{-29}	AuCl ₃	3.2×10^{-25}
Calcium compounds		Au(OH) ₃	1.0×10^{-53}
Ca ₃ (AsO ₄) ₂	6.8×10^{-19}	AuI ₃	1.0×10^{-46}
CaCO ₃	4.8×10^{-9}	Iron compounds	
CaCrO ₄	7.1×10^{-4}	FeCO ₃	3.5×10^{-11}
CaC ₂ O ₄ · H ₂ O*	2.3×10^{-9}	Fe(OH) ₂	7.9×10^{-15}
CaF ₂	3.9×10^{-11}	FeS	4.9×10^{-18}
Ca(OH) ₂	7.9×10^{-6}	Fe ₄ [Fe(CN) ₆] ₃	3.0×10^{-41}
CaHPO ₄	2.7×10^{-7}	Fe(OH) ₃	6.3×10^{-38}
Ca(H ₂ PO ₄) ₂	1.0×10^{-3}	Fe ₂ S ₃	1.4×10^{-88}
Ca ₃ (PO ₄) ₂	1.0×10^{-25}	Lead compounds	
CaSO ₃ · 2H ₂ O*	1.3×10^{-8}	Pb ₃ (AsO ₄) ₂	4.1×10^{-36}
CaSO ₄ · 2H ₂ O*	2.4×10^{-5}	PbBr ₂	6.3×10^{-6}

Substance	K_{sp}	Substance	K_{sp}
Lead compounds (cont.)		Nickel compounds (cont.)	
PbCO ₃	1.5×10^{-13}	NiS (α)	3.0×10^{-21}
PbCl ₂	1.7×10^{-5}	NiS (β)	1.0×10^{-26}
PbCrO ₄	1.8×10^{-14}	NiS (γ)	2.0×10^{-28}
PbF ₂	3.7×10^{-8}	Silver compounds	
Pb(OH) ₂	2.8×10^{-16}	Ag ₃ AsO ₄	1.1×10^{-20}
PbI ₂	8.7×10^{-9}	AgBr	3.3×10^{-13}
Pb ₃ (PO ₄) ₂	3.0×10^{-44}	Ag ₂ CO ₃	8.1×10^{-12}
PbSeO ₄	1.5×10^{-7}	AgCl	1.8×10^{-10}
PbSO ₄	1.8×10^{-8}	Ag ₂ CrO ₄	9.0×10^{-12}
PbS	8.4×10^{-28}	AgCN	1.2×10^{-16}
Magnesium compounds		Ag ₄ [Fe(CN) ₆]	1.6×10^{-41}
Mg ₃ (AsO ₄) ₂	2.1×10^{-20}	Ag ₂ O (Ag ⁺ + OH ⁻) [†]	2.0×10^{-8}
MgCO ₃ · 3H ₂ O*	4.0×10^{-5}	AgI	1.5×10^{-16}
MgC ₂ O ₄	8.6×10^{-5}	Ag ₃ PO ₄	1.3×10^{-20}
MgF ₂	6.4×10^{-9}	Ag ₂ SO ₃	1.5×10^{-14}
Mg(OH) ₂	1.5×10^{-11}	Ag ₂ SO ₄	1.7×10^{-5}
MgNH ₄ PO ₄	2.5×10^{-12}	Ag ₂ S	1.0×10^{-49}
Manganese compounds		AgSCN	1.0×10^{-12}
Mn ₃ (AsO ₄) ₂	1.9×10^{-11}	Strontium compounds	
MnCO ₃	1.8×10^{-11}	Sr ₃ (AsO ₄) ₂	1.3×10^{-18}
Mn(OH) ₂	4.6×10^{-14}	SrCO ₃	9.4×10^{-10}
MnS	5.1×10^{-15}	SrC ₂ O ₄ · 2H ₂ O*	5.6×10^{-8}
Mn(OH) ₃	$\approx 1.0 \times 10^{-36}$	SrCrO ₄	3.6×10^{-5}
Mercury compounds		Sr(OH) ₂ · 8H ₂ O*	3.2×10^{-4}
Hg ₂ Br ₂	1.3×10^{-22}	Sr ₃ (PO ₄) ₂	1.0×10^{-31}
Hg ₂ CO ₃	8.9×10^{-17}	SrSO ₃	4.0×10^{-8}
Hg ₂ Cl ₂	1.1×10^{-18}	SrSO ₄	2.8×10^{-7}
Hg ₂ CrO ₄	5.0×10^{-9}	Tin compounds	
Hg ₂ I ₂	4.5×10^{-29}	Sn(OH) ₂	2.0×10^{-26}
Hg ₂ O · H ₂ O*		SnI ₂	1.0×10^{-4}
(Hg ₂ ²⁺ + 2OH ⁻) [†]	1.6×10^{-23}	SnS	1.0×10^{-28}
Hg ₂ SO ₄	6.8×10^{-7}	Sn(OH) ₄	1.0×10^{-57}
Hg ₂ S	5.8×10^{-44}	SnS ₂	1.0×10^{-70}
Hg(CN) ₂	3.0×10^{-23}	Zinc compounds	
Hg(OH) ₂	2.5×10^{-26}	Zn ₃ (AsO ₄) ₂	1.1×10^{-27}
HgI ₂	4.0×10^{-29}	ZnCO ₃	1.5×10^{-11}
HgS	3.0×10^{-53}	Zn(CN) ₂	8.0×10^{-12}
Nickel compounds		Zn ₂ [Fe(CN) ₆]	4.1×10^{-16}
Ni ₃ (AsO ₄) ₂	1.9×10^{-26}	Zn(OH) ₂	4.5×10^{-17}
NiCO ₃	6.6×10^{-9}	Zn ₃ (PO ₄) ₂	9.1×10^{-33}
Ni(CN) ₂	3.0×10^{-23}	ZnS	1.1×10^{-21}
Ni(OH) ₂	2.8×10^{-16}		

*[H₂O] does not appear in equilibrium constants for equilibria in aqueous solution in general, so it does *not* appear in the K_{sp} expressions for hydrated solids.

[†]Very small amounts of oxides dissolve in water to give the ions indicated in parentheses. These solid hydroxides are unstable and decompose to oxides as rapidly as they are formed.

Dissociation Constants for Some Complex Ions

Dissociation Equilibrium	K_d
$[\text{AgBr}_2]^- \rightleftharpoons \text{Ag}^+ + 2\text{Br}^-$	7.8×10^{-8}
$[\text{AgCl}_2]^- \rightleftharpoons \text{Ag}^+ + 2\text{Cl}^-$	4.0×10^{-6}
$[\text{Ag}(\text{CN})_2]^- \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$	1.8×10^{-19}
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-} \rightleftharpoons \text{Ag}^+ + 2\text{S}_2\text{O}_3^{2-}$	5.0×10^{-14}
$[\text{Ag}(\text{NH}_3)_2]^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$	6.3×10^{-8}
$[\text{Ag}(\text{en})]^+ \rightleftharpoons \text{Ag}^+ + \text{en}^*$	1.0×10^{-5}
$[\text{AlF}_6]^{3-} \rightleftharpoons \text{Al}^{3+} + 6\text{F}^-$	2.0×10^{-24}
$[\text{Al}(\text{OH})_4]^- \rightleftharpoons \text{Al}^{3+} + 4\text{OH}^-$	1.3×10^{-34}
$[\text{Au}(\text{CN})_2]^- \rightleftharpoons \text{Au}^+ + 2\text{CN}^-$	5.0×10^{-39}
$[\text{Cd}(\text{CN})_4]^{2-} \rightleftharpoons \text{Cd}^{2+} + 4\text{CN}^-$	7.8×10^{-18}
$[\text{CdCl}_4]^{2-} \rightleftharpoons \text{Cd}^{2+} + 4\text{Cl}^-$	1.0×10^{-4}
$[\text{Cd}(\text{NH}_3)_4]^{2+} \rightleftharpoons \text{Cd}^{2+} + 4\text{NH}_3$	1.0×10^{-7}
$[\text{Co}(\text{NH}_3)_6]^{2+} \rightleftharpoons \text{Co}^{2+} + 6\text{NH}_3$	1.3×10^{-5}
$[\text{Co}(\text{NH}_3)_6]^{3+} \rightleftharpoons \text{Co}^{3+} + 6\text{NH}_3$	2.2×10^{-34}
$[\text{Co}(\text{en})_3]^{2+} \rightleftharpoons \text{Co}^{2+} + 3\text{en}^*$	1.5×10^{-14}
$[\text{Co}(\text{en})_3]^{3+} \rightleftharpoons \text{Co}^{3+} + 3\text{en}^*$	2.0×10^{-49}
$[\text{Cu}(\text{CN})_2]^- \rightleftharpoons \text{Cu}^+ + 2\text{CN}^-$	1.0×10^{-16}
$[\text{CuCl}_2]^- \rightleftharpoons \text{Cu}^+ + 2\text{Cl}^-$	1.0×10^{-5}
$[\text{Cu}(\text{NH}_3)_2]^+ \rightleftharpoons \text{Cu}^+ + 2\text{NH}_3$	1.4×10^{-11}
$[\text{Cu}(\text{NH}_3)_4]^{2+} \rightleftharpoons \text{Cu}^{2+} + 4\text{NH}_3$	8.5×10^{-13}
$[\text{Fe}(\text{CN})_6]^{4-} \rightleftharpoons \text{Fe}^{2+} + 6\text{CN}^-$	1.3×10^{-37}
$[\text{Fe}(\text{CN})_6]^{3-} \rightleftharpoons \text{Fe}^{3+} + 6\text{CN}^-$	1.3×10^{-44}
$[\text{HgCl}_4]^{2-} \rightleftharpoons \text{Hg}^{2+} + 4\text{Cl}^-$	8.3×10^{-16}
$[\text{Ni}(\text{CN})_4]^{2-} \rightleftharpoons \text{Ni}^{2+} + 4\text{CN}^-$	1.0×10^{-31}
$[\text{Ni}(\text{NH}_3)_6]^{2+} \rightleftharpoons \text{Ni}^{2+} + 6\text{NH}_3$	1.8×10^{-9}
$[\text{Zn}(\text{OH})_4]^{2-} \rightleftharpoons \text{Zn}^{2+} + 4\text{OH}^-$	3.5×10^{-16}
$[\text{Zn}(\text{NH}_3)_4]^{2+} \rightleftharpoons \text{Zn}^{2+} + 4\text{NH}_3$	3.4×10^{-10}

*The abbreviation “en” represents ethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.

Standard Reduction Potentials in Aqueous Solution at 25°C

Acidic Solution	Standard Reduction Potential, E^0 (volts)
$\text{Li}^+(\text{aq}) + e^- \longrightarrow \text{Li}(\text{s})$	-3.045
$\text{K}^+(\text{aq}) + e^- \longrightarrow \text{K}(\text{s})$	-2.925
$\text{Rb}^+(\text{aq}) + e^- \longrightarrow \text{Rb}(\text{s})$	-2.925
$\text{Ba}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Ba}(\text{s})$	-2.90
$\text{Sr}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Sr}(\text{s})$	-2.89
$\text{Ca}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Ca}(\text{s})$	-2.87
$\text{Na}^+(\text{aq}) + e^- \longrightarrow \text{Na}(\text{s})$	-2.714
$\text{Mg}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Mg}(\text{s})$	-2.37
$\text{H}_2(\text{g}) + 2e^- \longrightarrow 2\text{H}^-(\text{aq})$	-2.25
$\text{Al}^{3+}(\text{aq}) + 3e^- \longrightarrow \text{Al}(\text{s})$	-1.66
$\text{Zr}^{4+}(\text{aq}) + 4e^- \longrightarrow \text{Zr}(\text{s})$	-1.53
$\text{ZnS}(\text{s}) + 2e^- \longrightarrow \text{Zn}(\text{s}) + \text{S}^{2-}(\text{aq})$	-1.44
$\text{CdS}(\text{s}) + 2e^- \longrightarrow \text{Cd}(\text{s}) + \text{S}^{2-}(\text{aq})$	-1.21
$\text{V}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{V}(\text{s})$	-1.18
$\text{Mn}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Mn}(\text{s})$	-1.18
$\text{FeS}(\text{s}) + 2e^- \longrightarrow \text{Fe}(\text{s}) + \text{S}^{2-}(\text{aq})$	-1.01
$\text{Cr}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Cr}(\text{s})$	-0.91
$\text{Zn}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Zn}(\text{s})$	-0.763
$\text{Cr}^{3+}(\text{aq}) + 3e^- \longrightarrow \text{Cr}(\text{s})$	-0.74
$\text{HgS}(\text{s}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{Hg}(\ell) + \text{H}_2\text{S}(\text{g})$	-0.72
$\text{Ga}^{3+}(\text{aq}) + 3e^- \longrightarrow \text{Ga}(\text{s})$	-0.53
$2\text{CO}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow (\text{COOH})_2(\text{aq})$	-0.49
$\text{Fe}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+}(\text{aq}) + e^- \longrightarrow \text{Cr}^{2+}(\text{aq})$	-0.41
$\text{Cd}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Cd}(\text{s})$	-0.403
$\text{Se}(\text{s}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{H}_2\text{Se}(\text{aq})$	-0.40
$\text{PbSO}_4(\text{s}) + 2e^- \longrightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.356
$\text{Tl}^+(\text{aq}) + e^- \longrightarrow \text{Tl}(\text{s})$	-0.34
$\text{Co}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Co}(\text{s})$	-0.28
$\text{Ni}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Ni}(\text{s})$	-0.25
$[\text{SnF}_6]^{2-}(\text{aq}) + 4e^- \longrightarrow \text{Sn}(\text{s}) + 6\text{F}^-(\text{aq})$	-0.25

Acidic Solution	Standard Reduction Potential, E^0 (volts)
$\text{AgI(s)} + e^- \longrightarrow \text{Ag(s)} + \text{I}^-(\text{aq})$	-0.15
$\text{Sn}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Sn(s)}$	-0.14
$\text{Pb}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Pb(s)}$	-0.126
$\text{N}_2\text{O(g)} + 6\text{H}^+(\text{aq}) + \text{H}_2\text{O} + 4e^- \longrightarrow 2\text{NH}_3\text{OH}^+(\text{aq})$	-0.05
$2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{H}_2(\text{g})$ (reference electrode)	0.000
$\text{AgBr(s)} + e^- \longrightarrow \text{Ag(s)} + \text{Br}^-(\text{aq})$	0.10
$\text{S(s)} + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{H}_2\text{S(aq)}$	0.14
$\text{Sn}^{4+}(\text{aq}) + 2e^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$\text{Cu}^{2+}(\text{aq}) + e^- \longrightarrow \text{Cu}^+(\text{aq})$	0.153
$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}$	0.17
$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}$	0.20
$\text{AgCl(s)} + e^- \longrightarrow \text{Ag(s)} + \text{Cl}^-(\text{aq})$	0.222
$\text{Hg}_2\text{Cl}_2(\text{s}) + 2e^- \longrightarrow 2\text{Hg}(\ell) + 2\text{Cl}^-(\text{aq})$	0.27
$\text{Cu}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Cu(s)}$	0.337
$[\text{RhCl}_6]^{3-}(\text{aq}) + 3e^- \longrightarrow \text{Rh(s)} + 6\text{Cl}^-(\text{aq})$	0.44
$\text{Cu}^+(\text{aq}) + e^- \longrightarrow \text{Cu(s)}$	0.521
$\text{TeO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 4e^- \longrightarrow \text{Te(s)} + 2\text{H}_2\text{O}$	0.529
$\text{I}_2(\text{s}) + 2e^- \longrightarrow 2\text{I}^-(\text{aq})$	0.535
$\text{H}_3\text{AsO}_4(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{H}_3\text{AsO}_3(\text{aq}) + \text{H}_2\text{O}$	0.58
$[\text{PtCl}_6]^{2-}(\text{aq}) + 2e^- \longrightarrow [\text{PtCl}_4]^{2-}(\text{aq}) + 2\text{Cl}^-(\text{aq})$	0.68
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	0.682
$[\text{PtCl}_4]^{2-}(\text{aq}) + 2e^- \longrightarrow \text{Pt(s)} + 4\text{Cl}^-(\text{aq})$	0.73
$\text{SbCl}_6^-(\text{aq}) + 2e^- \longrightarrow \text{SbCl}_4^-(\text{aq}) + 2\text{Cl}^-(\text{aq})$	0.75
$\text{Fe}^{3+}(\text{aq}) + e^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	0.771
$\text{Hg}_2^{2+}(\text{aq}) + 2e^- \longrightarrow 2\text{Hg}(\ell)$	0.789
$\text{Ag}^+(\text{aq}) + e^- \longrightarrow \text{Ag(s)}$	0.7994
$\text{Hg}_2^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Hg}(\ell)$	0.855
$2\text{Hg}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Hg}_2^{2+}(\text{aq})$	0.920
$\text{NO}_3^-(\text{aq}) + 3\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{HNO}_2(\text{aq}) + \text{H}_2\text{O}$	0.94
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3e^- \longrightarrow \text{NO(g)} + 2\text{H}_2\text{O}$	0.96
$\text{Pd}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Pd(s)}$	0.987
$\text{AuCl}_4^-(\text{aq}) + 3e^- \longrightarrow \text{Au(s)} + 4\text{Cl}^-(\text{aq})$	1.00
$\text{Br}_2(\ell) + 2e^- \longrightarrow 2\text{Br}^-(\text{aq})$	1.08
$\text{ClO}_4^-(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{ClO}_3^-(\text{aq}) + \text{H}_2\text{O}$	1.19
$\text{IO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 5e^- \longrightarrow \frac{1}{2}\text{I}_2(\text{aq}) + 3\text{H}_2\text{O}$	1.195
$\text{Pt}^{2+}(\text{aq}) + 2e^- \longrightarrow \text{Pt(s)}$	1.2
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \longrightarrow 2\text{H}_2\text{O}$	1.229
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	1.23
$\text{N}_2\text{H}_5^+(\text{aq}) + 3\text{H}^+(\text{aq}) + 2e^- \longrightarrow 2\text{NH}_4^+(\text{aq})$	1.24
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6e^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	1.33
$\text{Cl}_2(\text{g}) + 2e^- \longrightarrow 2\text{Cl}^-(\text{aq})$	1.360
$\text{BrO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 6e^- \longrightarrow \text{Br}^-(\text{aq}) + 3\text{H}_2\text{O}$	1.44
$\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 5e^- \longrightarrow \frac{1}{2}\text{Cl}_2(\text{g}) + 3\text{H}_2\text{O}$	1.47
$\text{Au}^{3+}(\text{aq}) + 3e^- \longrightarrow \text{Au(s)}$	1.50

Unless otherwise noted, all content on this page is © Cengage Learning.

Basic Solution	Standard Reduction Potential, E^0 (volts)
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5e^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	1.507
$\text{NaBiO}_3(\text{s}) + 6\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{Bi}^{3+}(\text{aq}) + \text{Na}^+(\text{aq}) + 3\text{H}_2\text{O}$	1.6
$\text{Ce}^{4+}(\text{aq}) + e^- \longrightarrow \text{Ce}^{3+}(\text{aq})$	1.61
$2\text{HOCl}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}$	1.63
$\text{Au}^+(\text{aq}) + e^- \longrightarrow \text{Au}(\text{s})$	1.68
$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$	1.685
$\text{NiO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	1.7
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \longrightarrow 2\text{H}_2\text{O}$	1.77
$\text{Pb}^{4+}(\text{aq}) + 2e^- \longrightarrow \text{Pb}^{2+}(\text{aq})$	1.8
$\text{Co}^{3+}(\text{aq}) + e^- \longrightarrow \text{Co}^{2+}(\text{aq})$	1.82
$\text{F}_2(\text{g}) + 2e^- \longrightarrow 2\text{F}^-(\text{aq})$	2.87
$\text{SiO}_3^{2-}(\text{aq}) + 3\text{H}_2\text{O} + 4e^- \longrightarrow \text{Si}(\text{s}) + 6\text{OH}^-(\text{aq})$	-1.70
$\text{Cr}(\text{OH})_3(\text{s}) + 3e^- \longrightarrow \text{Cr}(\text{s}) + 3\text{OH}^-(\text{aq})$	-1.30
$[\text{Zn}(\text{CN})_4]^{2-}(\text{aq}) + 2e^- \longrightarrow \text{Zn}(\text{s}) + 4\text{CN}^-(\text{aq})$	-1.26
$\text{Zn}(\text{OH})_2(\text{s}) + 2e^- \longrightarrow \text{Zn}(\text{s}) + 2\text{OH}^-(\text{aq})$	-1.245
$[\text{Zn}(\text{OH})_4]^{2-}(\text{aq}) + 2e^- \longrightarrow \text{Zn}(\text{s}) + 4\text{OH}^-(\text{aq})$	-1.22
$\text{N}_2(\text{g}) + 4\text{H}_2\text{O} + 4e^- \longrightarrow \text{N}_2\text{H}_4(\text{aq}) + 4\text{OH}^-(\text{aq})$	-1.15
$\text{SO}_4^{2-}(\text{aq}) + \text{H}_2\text{O} + 2e^- \longrightarrow \text{SO}_3^{2-}(\text{aq}) + 2\text{OH}^-(\text{aq})$	-0.93
$\text{Fe}(\text{OH})_2(\text{s}) + 2e^- \longrightarrow \text{Fe}(\text{s}) + 2\text{OH}^-(\text{aq})$	-0.877
$2\text{NO}_3^-(\text{aq}) + 2\text{H}_2\text{O} + 2e^- \longrightarrow \text{N}_2\text{O}_4(\text{g}) + 4\text{OH}^-(\text{aq})$	-0.85
$2\text{H}_2\text{O} + 2e^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.828
$\text{Fe}(\text{OH})_3(\text{s}) + e^- \longrightarrow \text{Fe}(\text{OH})_2(\text{s}) + \text{OH}^-(\text{aq})$	-0.56
$\text{S}(\text{s}) + 2e^- \longrightarrow \text{S}^{2-}(\text{aq})$	-0.48
$\text{Cu}(\text{OH})_2(\text{s}) + 2e^- \longrightarrow \text{Cu}(\text{s}) + 2\text{OH}^-(\text{aq})$	-0.36
$\text{CrO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O} + 3e^- \longrightarrow \text{Cr}(\text{OH})_3(\text{s}) + 5\text{OH}^-(\text{aq})$	-0.12
$\text{MnO}_2(\text{s}) + 2\text{H}_2\text{O} + 2e^- \longrightarrow \text{Mn}(\text{OH})_2(\text{s}) + 2\text{OH}^-(\text{aq})$	-0.05
$\text{NO}_3^-(\text{aq}) + \text{H}_2\text{O} + 2e^- \longrightarrow \text{NO}_2^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.01
$\text{O}_2(\text{g}) + \text{H}_2\text{O} + 2e^- \longrightarrow \text{OOH}^-(\text{aq}) + \text{OH}^-(\text{aq})$	0.076
$\text{HgO}(\text{s}) + \text{H}_2\text{O} + 2e^- \longrightarrow \text{Hg}(\ell) + 2\text{OH}^-(\text{aq})$	0.0984
$[\text{Co}(\text{NH}_3)_6]^{3+}(\text{aq}) + e^- \longrightarrow [\text{Co}(\text{NH}_3)_6]^{2+}(\text{aq})$	0.10
$\text{N}_2\text{H}_4(\text{aq}) + 2\text{H}_2\text{O} + 2e^- \longrightarrow 2\text{NH}_3(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.10
$2\text{NO}_2^-(\text{aq}) + 3\text{H}_2\text{O} + 4e^- \longrightarrow \text{N}_2\text{O}(\text{g}) + 6\text{OH}^-(\text{aq})$	0.15
$\text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O} + 2e^- \longrightarrow 2\text{Ag}(\text{s}) + 2\text{OH}^-(\text{aq})$	0.34
$\text{ClO}_4^-(\text{aq}) + \text{H}_2\text{O} + 2e^- \longrightarrow \text{ClO}_3^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.36
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4e^- \longrightarrow 4\text{OH}^-(\text{aq})$	0.40
$\text{Ag}_2\text{CrO}_4(\text{s}) + 2e^- \longrightarrow 2\text{Ag}(\text{s}) + \text{CrO}_4^{2-}(\text{aq})$	0.446
$\text{NiO}_2(\text{s}) + 2\text{H}_2\text{O} + 2e^- \longrightarrow \text{Ni}(\text{OH})_2(\text{s}) + 2\text{OH}^-(\text{aq})$	0.49
$\text{MnO}_4^-(\text{aq}) + e^- \longrightarrow \text{MnO}_4^{2-}(\text{aq})$	0.564
$\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O} + 3e^- \longrightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$	0.588
$\text{ClO}_3^-(\text{aq}) + 3\text{H}_2\text{O} + 6e^- \longrightarrow \text{Cl}^-(\text{aq}) + 6\text{OH}^-(\text{aq})$	0.62
$2\text{NH}_2\text{OH}(\text{aq}) + 2e^- \longrightarrow \text{N}_2\text{H}_4(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.74
$\text{OOH}^-(\text{aq}) + \text{H}_2\text{O} + 2e^- \longrightarrow 3\text{OH}^-(\text{aq})$	0.88
$\text{ClO}^-(\text{aq}) + \text{H}_2\text{O} + 2e^- \longrightarrow \text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.89

Selected Thermodynamic Values at 298.15 K

APPENDIX

K

Species	ΔH_f° (kJ/mol)	S° (J/mol · K)	ΔG_f° (kJ/mol)	Species	ΔH_f° (kJ/mol)	S° (J/mol · K)	ΔG_f° (kJ/mol)
Aluminum				CHCl ₃ (g)	−103.1	295.6	−70.37
Al(s)	0	28.3	0	CH ₄ (g)	−74.81	186.2	−50.75
AlCl ₃ (s)	−704.2	110.7	−628.9	C ₂ H ₂ (g)	226.7	200.8	209.2
Al ₂ O ₃ (s)	−1676	50.92	−1582	C ₂ H ₄ (g)	52.26	219.5	68.12
Barium				C ₂ H ₆ (g)	−84.86	229.5	−32.9
BaCl ₂ (s)	−860.1	126	−810.9	C ₃ H ₈ (g)	−103.8	269.9	−23.49
BaSO ₄ (s)	−1465	132	−1353	C ₆ H ₆ (ℓ)	49.03	172.8	124.5
Beryllium				C ₈ H ₁₈ (ℓ)	−268.8	—	—
Be(s)	0	9.54	0	C ₂ H ₅ OH(ℓ)	−277.7	161	−174.9
Be(OH) ₂ (s)	−907.1	—	—	C ₂ H ₅ OH(g)	−235.1	282.6	−168.6
Bromine				CO(g)	−110.5	197.6	−137.2
Br(g)	111.8	174.9	82.4	CO ₂ (g)	−393.5	213.6	−394.4
Br ₂ (ℓ)	0	152.23	0	CS ₂ (g)	117.4	237.7	67.15
Br ₂ (g)	30.91	245.4	3.14	COCl ₂ (g)	−223.0	289.2	−210.5
BrF ₃ (g)	−255.6	292.4	−229.5	Cesium			
HBr(g)	−36.4	198.59	−53.43	Cs ⁺ (aq)	−248	133	−282.0
Calcium				CsF(aq)	−568.6	123	−558.5
Ca(s)	0	41.6	0	Chlorine			
Ca(g)	192.6	154.8	158.9	Cl(g)	121.7	165.1	105.7
Ca ²⁺ (g)	1920	—	—	Cl [−] (g)	−226	—	—
CaC ₂ (s)	−62.8	70.3	−67.8	Cl ₂ (g)	0	223.0	0
CaCO ₃ (s)	−1207	92.9	−1129	HCl(g)	−92.31	186.8	−95.30
CaCl ₂ (s)	−795.0	114	−750.2	HCl(aq)	−167.4	55.10	−131.2
CaF ₂ (s)	−1215	68.87	−1162	Chromium			
CaH ₂ (s)	−189	42	−150	Cr(s)	0	23.8	0
CaO(s)	−635.5	40	−604.2	(NH ₄) ₂ Cr ₂ O ₇ (s)	−1807	—	—
CaS(s)	−482.4	56.5	−477.4	Copper			
Ca(OH) ₂ (s)	−986.6	76.1	−896.8	Cu(s)	0	33.15	0
Ca(OH) ₂ (aq)	−1002.8	76.15	−867.6	CuO(s)	−157	42.63	−130
CaSO ₄ (s)	−1433	107	−1320	Fluorine			
Carbon				F [−] (g)	−322	—	—
C(s, graphite)	0	5.740	0	F [−] (aq)	−332.6	—	−278.8
C(s, diamond)	1.897	2.38	2.900	F(g)	78.99	158.6	61.92
C(g)	716.7	158.0	671.3	F ₂ (g)	0	202.7	0
CCl ₄ (ℓ)	−135.4	216.4	−65.27	HF(g)	−271	173.7	−273
CCl ₄ (g)	−103	309.7	−60.63	HF(aq)	−320.8	—	−296.8
CHCl ₃ (ℓ)	−134.5	202	−73.72				

Species	ΔH_f° (kJ/mol)	S° (J/mol · K)	ΔG_f° (kJ/mol)	Species	ΔH_f° (kJ/mol)	S° (J/mol · K)	ΔG_f° (kJ/mol)
Hydrogen				NH ₄ Cl(s)	−314.4	94.6	−201.5
H(g)	218.0	114.6	203.3	NH ₄ Cl(aq)	−300.2	—	—
H ₂ (g)	0	130.6	0	NH ₄ I(s)	−201.4	117	−113
H ₂ O(ℓ)	−285.8	69.91	−237.2	NH ₄ NO ₃ (s)	−365.6	151.1	−184.0
H ₂ O(g)	−241.8	188.7	−228.6	NO(g)	90.25	210.7	86.57
H ₂ O ₂ (ℓ)	−187.8	109.6	−120.4	NO ₂ (g)	33.2	240.0	51.30
Iodine				N ₂ O(g)	82.05	219.7	104.2
I(g)	106.6	180.66	70.16	N ₂ O ₄ (g)	9.16	304.2	97.82
I ₂ (s)	0	116.1	0	N ₂ O ₅ (g)	11	356	115
I ₂ (g)	62.44	260.6	19.36	N ₂ O ₅ (s)	−43.1	178	114
ICl(g)	17.78	247.4	−5.52	NOCl(g)	52.59	264	66.36
HI(g)	26.5	206.5	1.72	HNO ₃ (ℓ)	−174.1	155.6	−80.79
Iron				HNO ₃ (g)	−135.1	266.2	−74.77
Fe(s)	0	27.3	0	HNO ₃ (aq)	−206.6	146	−110.5
FeO(s)	−272	—	—	Oxygen			
Fe ₂ O ₃ (s, hematite)	−824.2	87.40	−742.2	O(g)	249.2	161.0	231.8
Fe ₃ O ₄ (s, magnetite)	−1118	146	−1015	O ₂ (g)	0	205.0	0
FeS ₂ (s)	−177.5	122.2	−166.7	O ₃ (g)	143	238.8	163
Fe(CO) ₅ (ℓ)	−774.0	338	−705.4	OF ₂ (g)	23	246.6	41
Fe(CO) ₅ (g)	−733.8	445.2	−697.3	Phosphorus			
Lead				P(g)	314.6	163.1	278.3
Pb(s)	0	64.81	0	P ₄ (s, white)	0	177	0
PbCl ₂ (s)	−359.4	136	−314.1	P ₄ (s, red)	−73.6	91.2	−48.5
PbO(s, yellow)	−217.3	68.70	−187.9	PCl ₃ (g)	−306.4	311.7	−286.3
Pb(OH) ₂ (s)	−515.9	88	−420.9	PCl ₅ (g)	−398.9	353	−324.6
PbS(s)	−100.4	91.2	−98.7	PH ₃ (g)	5.4	210.1	13
Lithium				P ₄ O ₁₀ (s)	−2984	228.9	−2698
Li(s)	0	28.0	0	H ₃ PO ₄ (s)	−1281	110.5	−1119
LiOH(s)	−487.23	50	−443.9	Potassium			
LiOH(aq)	−508.4	4	−451.1	K(s)	0	63.6	0
Magnesium				KCl(s)	−436.5	82.6	−408.8
Mg(s)	0	32.5	0	KClO ₃ (s)	−391.2	143.1	−289.9
MgCl ₂ (s)	−641.8	89.5	−592.3	KI(s)	−327.9	106.4	−323.0
MgO(s)	−601.8	27	−569.6	KOH(s)	−424.7	78.91	−378.9
Mg(OH) ₂ (s)	−924.7	63.14	−833.7	KOH(aq)	−481.2	92.0	−439.6
MgS(s)	−347	—	—	Rubidium			
Mercury				Rb(s)	0	76.78	0
Hg(ℓ)	0	76.02	0	RbOH(aq)	−481.16	110.75	−441.24
HgCl ₂ (s)	−224	146	−179	Silicon			
HgO(s, red)	−90.83	70.29	−58.56	Si(s)	0	18.8	0
HgS(s, red)	−58.2	82.4	−50.6	SiBr ₄ (ℓ)	−457.3	277.8	−443.9
Nickel				SiC(s)	−65.3	16.6	−62.8
Ni(s)	0	30.1	0	SiCl ₄ (g)	−657.0	330.6	−617.0
Ni(CO) ₄ (g)	−602.9	410.4	−587.3	SiH ₄ (g)	34.3	204.5	56.9
NiO(s)	−244	38.6	−216	SiF ₄ (g)	−1615	282.4	−1573
Nitrogen				SiL ₄ (g)	−132	—	—
N ₂ (g)	0	191.5	0	SiO ₂ (s)	−910.9	41.84	−856.7
N(g)	472.704	153.19	455.579	H ₂ SiO ₃ (s)	−1189	134	−1092
NH ₃ (g)	−46.11	192.3	−16.5	Na ₂ SiO ₃ (s)	−1079	—	—
N ₂ H ₄ (ℓ)	50.63	121.2	149.2	H ₂ SiF ₆ (aq)	−2331	—	—
(NH ₄) ₃ AsO ₄ (aq)	−1268	—	—	Silver			
				Ag(s)	0	42.55	0

Unless otherwise noted, all content on this page is © Cengage Learning.

Species	ΔH_f° (kJ/mol)	S° (J/mol · K)	ΔG_f° (kJ/mol)	Species	ΔH_f° (kJ/mol)	S° (J/mol · K)	ΔG_f° (kJ/mol)
Sodium				H ₂ SO ₄ (ℓ)	−814.0	156.9	−690.1
Na(s)	0	51.0	0	H ₂ SO ₄ (aq)	−907.5	17	−742.0
Na(g)	108.7	153.6	78.11	Tin			
Na ⁺ (g)	601	—	—	Sn(s, white)	0	51.55	0
NaBr(s)	−359.9	—	—	Sn(s, grey)	−2.09	44.1	0.13
NaCl(s)	−411.0	72.38	−384	SnCl ₂ (s)	−350	—	—
NaCl(aq)	−407.1	115.5	−393.0	SnCl ₄ (ℓ)	−511.3	258.6	−440.2
Na ₂ CO ₃ (s)	−1131	136	−1048	SnCl ₄ (g)	−471.5	366	−432.2
NaOH(s)	−426.7	—	—	SnO ₂ (s)	−580.7	52.3	−519.7
NaOH(aq)	−469.6	49.8	−419.2	Titanium			
Sulfur				TiCl ₄ (ℓ)	−804.2	252.3	−737.2
S(s, rhombic)	0	31.8	0	TiCl ₄ (g)	−763.2	354.8	−726.8
S(g)	278.8	167.8	238.3	Tungsten			
S ₂ Cl ₂ (g)	−18	331	−31.8	W(s)	0	32.6	0
SF ₆ (g)	−1209	291.7	−1105	WO ₃ (s)	−842.9	75.90	−764.1
H ₂ S(g)	−20.6	205.7	−33.6	Zinc			
SO ₂ (g)	−296.8	248.1	−300.2	ZnO(s)	−348.3	43.64	−318.3
SO ₃ (g)	−395.6	256.6	−371.1	ZnS(s)	−205.6	57.7	−201.3
SOCl ₂ (ℓ)	−206	—	—				
SO ₂ Cl ₂ (ℓ)	−389	—	—				

L

Answers to Selected Even-Numbered Numerical Exercises

Chapter 1

30. (a) $423.006 \text{ mL} = 4.23006 \times 10^2 \text{ mL}$ (6 sig. fig.)
(b) $0.001073040 \text{ g} = 1.073040 \times 10^{-3} \text{ g}$ (7 sig. fig.)
(c) $1.08102 \text{ pounds} = 1.08102 \times 10^3 \text{ pounds}$ (6 sig. fig.)
32. (a) 50600 (b) 0.0004060 (c) 0.1610 (d) 0.000206 (e) 90000. (f) 0.0009000
34. $3.0 \times 10^4 \text{ cm}^3$
36. (a) 0.4534 km (b) $3.63 \times 10^4 \text{ m}$ (c) $4.87 \times 10^5 \text{ g}$ (d) $1.32 \times 10^3 \text{ mL}$ (e) 5.59 L (f) $6.251 \times 10^6 \text{ cm}^3$
38. 82.42 cents/L
40. (a) 21.2 L (b) 2.11 pt (c) 0.4252 km/L
42. 57.3%
44. (a) 9.0 qt (b) 88.5 km/hr (c) 73 s
46. 1.65 g/cm^3
48. (a) 42.2 cm^3 (b) 3.48 cm (c) 1.37 in
50. 504 m
52. $3.2 \times 10^2 \text{ g}$
54. (a) -9.4°C (b) 273.8 K (c) 130°F (d) 52.3°F
56. (c) 285.3°R
58. For Al, 660.4°C and 1221°F ; for Ag, 961.9°C and 1763°F
60. 39.8°C , 312.1 K
62. 1440 J
64. (a) $9.12 \times 10^5 \text{ J}$ (b) 11.8°C
66. $0.49 \text{ J/g}^\circ\text{C}$
68. (a) 62.7 tons of ore (b) 69.3 kg of ore
70. 7.16 m
72. 110 mg drug (2 sig. fig.)
74. 500 mL (1 sig. fig.)
84. $4.79 \times 10^7 \text{ atoms}$

Chapter 2

24. 1.070
28. (a) 159.808 amu (b) 34.014 amu (c) 183.18 amu (d) 194.189 amu
30. (a) 34.08 amu (b) 137.3 amu (c) 52.46 amu (d) 127.91 amu
32. 364.7 g CCl_4 , 0.3647 kg CCl_4
34. $1.82 \times 10^{25} \text{ H atoms}$
36. (a) 0.7340 mol NH_3
38. (a) $4.32 \times 10^{23} \text{ molecules CO}_2$ (b) $6.79 \times 10^{23} \text{ molecules N}_2$ (c) $1.53 \times 10^{23} \text{ molecules P}_4$ (d) $3.07 \times 10^{23} \text{ molecules P}_2$

44. $1.59 \times 10^{-16} \text{ g CH}_4$
48. 78.25% Ag
50. (a) $\text{C}_9\text{H}_9\text{N}$ (b) 131.2 g/mol
52. (a) $\text{C}_{13}\text{H}_{24}\text{N}_4\text{O}_3\text{S}$ (FW = 316 g/mol) (b) same
54. $\text{C}_8\text{H}_{11}\text{O}_3\text{N}$
56. NaHCO_3
58. $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$
60. C_2O_2
62. (a) 54.82% C, 5.624% H, 7.104% N, 32.45% O (b) 80.87% C, 11.70% H, 7.430% O (c) 63.15% C, 5.300% H, 31.55% O
64. $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ is 55.31% Cu, Cu_2S is 79.84% Cu, CuFeS_2 is 34.63% Cu, CuS is 66.47% Cu, Cu_2O is 88.82% Cu, $\text{Cu}_2\text{CO}_3(\text{OH})_2$ is 57.49% Cu
66. 0.1088 g C and 0.00647 g H giving 94.36% C and 5.61% H
68. 0.720 g CO_2
70. $\text{C}_2\text{H}_6\text{O}$
72. (a) 3.43 g O (b) 6.86 g O
74. (a) 9.02 g O (b) 13.5 g O
76. 498 g Hg
78. 209 g KMnO_4
80. 181 lb Cu_2S
82. (a) 352 g $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ (b) 296 g CuSO_4
84. 49.2 g Cr in ore, 75.7 g Cr recovered
86. (a) 73.4 lb MgCO_3 (b) 202 lb impurity (c) 21.2 lb Mg
88. (a) 63.92% (b) 47.6%
90. (a) 2.00 mol O_3 (b) 6.00 mol O (c) 96.0 g O_2 (d) 64.0 g O_2
92. $\text{C}_{14}\text{H}_{24}\text{O}$
96. (a) $\text{C}_3\text{H}_5\text{O}_2$ (b) $\text{C}_6\text{H}_{10}\text{O}_4$
102. ReO_2 (85.3358% Re^{+4}), ReO_3 (79.5063% Re^{+6}), Re_2O_3 (88.5833% Re^{+3}), Re_2O_7 (76.8804% Re^{+7})
104. $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OCH_3 will produce the most water
106. 261 g NaCl
108. ZnSO_4 is 35.95% more economical
110. (a) 844 g (b) $4.12 \times 10^3 \text{ g}$ (c) $3.84 \times 10^3 \text{ g}$
112. $\text{C}_3\text{H}_6\text{O}_2$, $\text{C}_3\text{H}_6\text{O}_2$
114. 1230 mL ethanol
116. (a) 2.16 g/mL (b) 4.930 g/mL (c) 13.59 g/mL (d) 2.165 g/mL

Chapter 3

12. (b) 450. molecules H_2 (c) 300. molecules NH_3
14. (b) 5.2 mol HCl (c) 2.6 mol H_2O
16. 882 g NaHCO_3 (to 3 sig. fig.)
18. (a) 9.6 mol O_2 (b) 3.2 mol O_2 (c) 3.2 mol O_2
(d) 3.2 mol O_2 (e) 13 mol O_2
20. (a) 8.00 mol O_2 (b) 6.40 mol NO (c) 9.60 mol H_2O
22. 178 g O_2
24. 87.22 g Fe_3O_4
26. (b) 55.80 g NaI
28. 79.9 g C_3H_8
30. (c) 211.59 g CO_2
32. 326.5 g superphosphate
34. (a) S_8 (b) 67.4 g S_2Cl_2 (c) 35.6 g Cl_2
36. 18.0 g $\text{Ca}_3(\text{PO}_4)_2$
38. (a) AgNO_3 (b) 14.9 g BaCl_2 (c) 52.7 g AgCl
40. 107 g PCl_5
42. (a) 2.27 g O_2 (b) 46.3%
44. 95.3%
46. 74.5%
48. (a) 349.7 g Fe (b) 47.61%
50. 82.6 g H_2TeO_3
52. 803.9 g KClO_3
54. (b) 2 mol N atoms (c) 106.4 g NH_3
56. 252 kg Zn
58. 149 g $(\text{NH}_4)_2\text{SO}_4$
60. 631 mL $(\text{NH}_4)_2\text{SO}_4$ soln
62. 0.866 M Na_3PO_4
64. 5.08×10^3 mL
66. (a) 20.0% CaCl_2 (b) 2.13 M CaCl_2
68. 0.00940 M BaCl_2 soln
70. 28.7 M HF soln
72. 0.250 L conc. HCl soln
76. 231 mL NaOH soln
78. 0.0408 L KOH soln
80. 8.41 mL HNO_3 soln
82. 0.00453 M AlCl_3 soln
84. 3.89% Fe_3O_4 in ore
86. 1.42 g Br_2
92. 3 mol Be , 0.966 g Be
94. 1.0% $\text{SnCl}_2 < 1.0\% \text{AlCl}_3 < 1.0\% \text{NaCl}$ in molarity
96. 68.0 mL HNO_3
100. (a) 62.7% yield
104. (a) $\text{CH}_3\text{CH}_2\text{OH}$ (b) 81.6% yield
106. 0.522 M NaCl
108. 623 g H_3PO_4
110. 0.0867 g AgCl
112. for Zn : \$65.4/mol H_2 ; for Al : \$36.0/mol H_2

Chapter 4

6. The charge on each droplet is a multiple of 1.22×10^{-19} coulombs
10. 2.3×10^{-14}
14. (a) mass % for $e^- = 0.026265\%$ (b) mass % for $p = 48.228\%$ (c) mass % for $n = 51.745\%$
26. ^{69}Ga : 60.13%; ^{71}Ga : 39.87%

28. 87.61 amu
30. 55.85 amu
32. 69.17% ^{63}Cu
34. O, 15.999 amu; Cl, 35.453 amu
36. 73.3 amu
38. 52.0 amu
54. (a) $3.34 \times 10^{14} \text{ s}^{-1}$ (b) $6.79 \times 10^{14} \text{ s}^{-1}$
(c) $6.10 \times 10^9 \text{ s}^{-1}$ (d) $6.59 \times 10^{18} \text{ s}^{-1}$
56. (a) $4.47 \times 10^{14} \text{ s}^{-1}$ (b) $2.96 \times 10^{-19} \text{ J/photon}$ (c) red
58. $5.85 \times 10^{-19} \text{ J/photon}$, 352 kJ/mol
60. 2.5×10^{13} miles
64. 320 nm (violet/near ultraviolet)
68. 218 kJ/mol
70. $3.20 \times 10^{15} \text{ s}^{-1}$
74. 2.53×10^{18} photons
76. (a) $1.59 \times 10^{-14} \text{ m}$ (b) $3.97 \times 10^{-34} \text{ m}$
78. $1.88 \times 10^3 \text{ m/s}$
122. (a) $n=3, \ell=1, m=-1, 0, +1$ (b) $n=6, \ell=2, m=-2, -1, 0, +1, +2$ (c) $n=3, \ell=1, m=-1, 0, +1$ (d) $n=4, \ell=3, m=-3, -2, -1, 0, +1, +2, +3$
132. 14.8 miles
136. 6 electrons
144. $3.76 \times 10^{-36} \text{ kg}$
146. 216 kJ/mol
148. 3.35 m
150. (a) 8.43×10^{24} electrons (b) 1.00×10^{25} electrons

Chapter 5

46. (a) oxidation no. of P: in PCl_3 , +3; in P_2O_5 , +5; in P_4O_{10} , +5; in HPO_3 , +5; in H_3PO_3 , +3; in POCl_3 , +5; in $\text{H}_4\text{P}_2\text{O}_7$, +5; in $\text{Mg}_3(\text{PO}_4)_2$, +5 (b) oxidation no. of Br: in Br^- , -1; in BrO^- , +1; in BrO_2^- , +3; in BrO_3^- , +5; in BrO_4^- , +7 (c) oxidation no. of Mn: in MnO , +2; in MnO_2 , +4; in $\text{Mn}(\text{OH})_2$, +2; in K_2MnO_4 , +6; in KMnO_4 , +7; in Mn_2O_7 , +7 (d) oxidation no. of O: in OF_2 , +2; in Na_2O , -2; in Na_2O_2 , -1; in KO_2 , -1/2
48. (a) oxidation no. of N: in N^{3-} , -3; in NO_2^- , +3; in NO_3^- , +5; in N_3^- , -1/3; in NH_4^+ , -3 (b) oxidation no. of Cl: in Cl_2 , 0; in HCl , -1; in HClO , +1; in HClO_2 , +3; in KClO_3 , +5; in Cl_2O_7 , +7; in $\text{Ca}(\text{ClO}_4)_2$, +7, in PCl_5 , -1
80. 122 pm
90. $1.05 \times 10^{15} \text{ s}^{-1}$
92. 158 kJ

Chapter 6

128. (a) 0.294 mol (b) 0.353 mol, 0.0554 mol

Chapters 7 and 8

No numerical exercises in these chapters.

Chapter 9

20. (a) Ne_2^+ , bo = 0.5 (b) Ne_2 , bo = 0 (c) Ne_2^{2+} , bo = 1
22. (a) Li_2 , bo = 1 (b) Li_2^+ , bo = 0.5 (c) O_2^{2-} , bo = 1
24. (a) X_2 , bo = 3 (b) X_2 , bo = 0 (c) X_2^- , bo = 2.5
28. (b) N_2 , bo = 3, N_2^- , bo = 2.5, N_2^+ , bo = 2.5
30. NO^+ , bo = 3

32. CN, bo = 2.5; CN⁺, bo = 2.0; CN²⁺, bo = 1.5; CN⁻, bo = 3; CN²⁻, bo = 2.5
 46. NO, bo = 2.5; NO⁺, bo = 3; NO⁻, bo = 2. Bond lengths are inversely related to bond order.

Chapter 10

No numerical problems in this chapter.

Chapter 11

4. 0.115 M MgSO₄
 6. 5.292 M H₂SO₄
 8. 1.16 M NaCl
 10. 5.49 M KI
 12. 0.0375 M BaI₂
 14. 1.35 M Na₃PO₄, 0.137 M NaOH
 16. 0.857 M CH₃COOH
 18. (a) 0.923 L NaOH soln, 0.222 L H₃PO₄ soln
 (b) 0.615 L NaOH soln, 0.222 L H₃PO₄ soln
 24. 31.3 mL of CH₃COOH soln
 26. 0.1969 M HNO₃
 28. 0.07321 M NaOH
 30. 18.0 mL HCl soln
 34. 36.0% (COOH)₂·2H₂O
 36. 0.150 g CaCO₃
 38. 0.0310 M NaOH
 40. 0.0539 M H₃PO₄, 32.5 mL H₃PO₄
 42. 0.13 M H₃AsO₄, 14 mL H₃AsO₄
 44. 0.233 M HCl
 46. 32.7% Mg(OH)₂
 52. oxidizing agents: (a) MnO₄⁻ (b) Cr₂O₇²⁻ (c) MnO₄⁻
 (d) Cr₂O₇²⁻
 62. 3.22 mL KMnO₄ soln
 64. 4.26 mL KMnO₄ soln
 66. (a) 0.09247 M I₂ (b) 0.3230 g As₂O₃
 68. 3.5 mL NO₃⁻ soln
 70. 0.123 M KMnO₄
 72. (a) 1.80×10^{-3} M MgNH₄PO₄ (b) 0.683 M NaCH₃COO (c) 2.60×10^{-4} M CaC₂O₄
 (d) 0.0416 M (NH₄)₂SO₄
 74. 7.60 mmol HCl, 12.5 mL HCl
 76. 463 mL HCl soln
 78. 17.2 mL H₂SO₄ soln
 80. 30.94 mL NaOH soln
 82. (a) 10.2 mL HI soln (b) 12.1 mL HI soln
 (c) 31.8 mL HI soln
 88. 59.36% Fe
 90. 69 g AgCl
 92. 80. mmol HCl in stomach; 9.28 mmol HCl

Chapter 12

6. (a) 14.4 psi (b) 74.2 cm Hg (c) 29.2 in Hg (d) 98.9 kPa
 (e) 0.976 atm (f) 33.1 ft H₂O
 10. 2.20×10^3 psi
 14. 1.06 atm
 16. (a) 18.2 atm (b) 0.274 L
 18. 6.0×10^2 balloons
 26. 0.81 L
 28. (a) 1.441 L (b) increase by 41 cm

30. -78.5°C, 3.26 L; -195.8°C, 1.30 L; -268.9°C, 0.0713 L
 34. 610. K or 337°C
 40. 5.23 g/L
 42. (a) #1 – Kr, #2 – Ne
 46. 5.20 atm
 48. (a) 1.75×10^8 L Cl₂, 6.18×10^6 ft³ Cl₂ (b) 39.0 ft
 50. 0.88 g He
 52. 22.0 L/mol for SF₆, 21.7 L/mol for HF
 54. 29.6 g/mol, 2% error
 56. 30.0 g/mol, C₂H₆(g)
 58. 46.7 amu/molecule
 62. $P_{\text{total}} = 92.8$ atm, $P_{\text{CHCl}_3} = 24.4$ atm
 64. $X_{\text{He}} = 0.440$, $X_{\text{Ar}} = 0.299$, $X_{\text{Xe}} = 0.261$
 66. (a) 11.25 atm (b) 3.75 atm (c) 3.75 atm
 68. 285 mL
 70. (a) He, 4.00 atm; N₂, 1.00 atm (b) 5.00 atm
 (c) X_{He} , 0.800
 72. 62.0 g NaN₃
 74. 7.15 g SO₂
 76. 4.45 g KClO₃
 78. 4.67 L NH₃
 80. 190. g KNO₃
 82. 25.1% S by mass
 84. (a) 2.83 L C₈H₁₈ (b) 44.8 min
 90. (b) 1.17
 98. (a) 0.821 atm (b) 0.805 atm (c) 18.1 atm, 13.6 atm
 100. (a) 7.34 atm (b) 7.14 atm
 102. liquid Fe: 8.12 cm³/mol, solid Fe: 7.11 cm³/mol
 104. 0.13 g H₂O
 106. 5000 L air (1 sig. fig.)
 108. 121 g/mol
 112. (a) 6130 g H₂O (b) 6150 mL H₂O
 114. 4.90 atm, 4.78 atm, 2.4%
 116. C₂N₂ (MW = 52.1 g/mol)
 118. 38°F, 22°C, 40K
 120. 1.106 g
 128. 2.1×10^{15} atoms Xe
 132. H₂ is the limiting reactant
 134. 1.3 L O₂
 136. 206 g MgSiO₃
 138. (a) 2.11×10^{-6} M SO₂ (b) 4.74×10^{-5}

Chapter 13

36. bp = ~34°C.
 40. (a) 43.4 kJ/mol
 42. bp = ~ -1°C
 44. 2.7×10^4 J
 48. boiling Br₂ (9660 J)
 50. 2.48×10^5 J
 52. 52.6°C
 54. 58.7°C
 56. (a) 6.14×10^3 J (b) 19.2 g H₂O
 58. for H₂O, 361.8 torr; for D₂O, 338.0 torr
 60. (c) $\Delta H_{\text{vap}} = 3.72 \times 10^4$ J/mol (d) 3.48×10^2 K or 75°C
 62. 4.34×10^4 J or 43.4 kJ
 64. 2.93×10^{-3} torr

88. (a) $a/2$ (b) 6 Cl^- ions (c) $a(2^{1/2})/2$ (d) 6 Na^+ ions
 90. 1.00 g/cm^3
 92. 22.4 g/cm^3
 94. (a) 8 (b) tetrahedron with 4 nearest neighbors
 (c) $\sqrt{3}(a/4)$ (d) $1.545 \text{ \AA}$ (e) 3.515 g/cm^3
 96. $\text{AW} = (1.37 \times 10^{-21} \text{ g})/(6.64 \times 10^{-24} \text{ mol}) = 206 \text{ g/mol}$, Pb (207.2 g/mol)
 100. $1.542 \text{ \AA}$
 112. (a) true (b) false (c) false
 114. $\text{CS}_2 < \text{acetone} < \text{ethanol}$
 130. 63 g/mol , Cu
 136. deviation at $0^\circ\text{C} = 0.9\%$, deviation at $100^\circ\text{C} = 0.8\%$

Chapter 14

18. X_{CH_4} (at 25°C) = 2.4×10^{-4} ; X_{CH_4} (at 50°C) = 1.7×10^{-4} ; decreases
 26. $0.886 \text{ m C}_{10}\text{H}_{16}\text{O}$; $X_{\text{C}_{10}\text{H}_{16}\text{O}} = 0.0393$; 11.9%
 28. $1.7 \text{ m C}_6\text{H}_5\text{COOH}$ in $\text{C}_2\text{H}_5\text{OH}$
 30. $X_{\text{C}_2\text{H}_5\text{OH}} = 0.322$; $X_{\text{H}_2\text{O}} = 0.678$
 32. $0.7767 \text{ M K}_2\text{SO}_4$, $0.8197 \text{ m K}_2\text{SO}_4$, $12.50\% \text{ K}_2\text{SO}_4$, $X_{\text{H}_2\text{O}} = 0.9854$
 34. (a) $1.48 \text{ m C}_6\text{H}_{12}\text{O}_6$
 38. (a) 14.12 torr (b) 16.72 torr (c) 19.00 torr
 40. $P_{\text{acetone}} = 172 \text{ torr}$, $P_{\text{chloroform}} = 148 \text{ torr}$
 42. $P_{\text{total}} = 320. \text{ torr}$, $X_{\text{acetone}} = 0.538$, $X_{\text{chloroform}} = 0.462$
 44. (a) $P_{\text{chloroform}} = 65 \text{ torr}$ (b) $P_{\text{acetone}} = 215 \text{ torr}$
 (c) $P_{\text{total}} = 280 \text{ torr}$
 46. 101.52°C
 48. -5.52°C
 50. (a) camphor (b) water (c) camphor (d) nitrobenzene
 52. -18.6°C
 54. 78.54°C
 56. 1035°C
 58. 170 g/mol
 60. $\text{C}_2\text{H}_8\text{O}_2$ (64.08 g/mol)
 62. (a) $70.0\% \text{ C}_{10}\text{H}_8$, $30.0\% \text{ C}_{14}\text{H}_{10}$ (b) 80.4°C
 66. (a) 3 (b) 2 (c) 5 (d) 2
 68. $\text{CaCl}_2 < \text{KClO}_3 < \text{CH}_3\text{COOH} < \text{CH}_3\text{OH}$ (based on i)
 70. 752 torr
 72. $0.100 \text{ m Na}_2\text{SO}_4$ has lower fp
 76. 100.247°C
 78. 1%
 80. $i = 1.79$, 79%
 84. 0.571 atm
 86. $\Delta T_f = 0.100^\circ\text{C}$, $\Delta T_b = 0.0276^\circ\text{C}$
 88. 58.0 atm
 90. (a) $-1.02 \times 10^{-4}^\circ\text{C}$ (b) $1.35 \times 10^{-3} \text{ atm}$ or 1.02 torr
 (c) 1000% error (d) 10% error
 98. bp = 100.44°C ; $\pi = 20.5 \text{ atm}$
 100. (a) 60.5 g/mol (b) 117 g/mol
 104. 37% lactose by mass
 108. For water: 215 mL , 215 g , 11.9 mol ; for ethanol: 285 mL , 225 g , 4.88 mol ; for glycerol: $630. \text{ g}$, 6.84 mol ;
 $X_{\text{water}} = 0.504$, $X_{\text{ethanol}} = 0.207$, $X_{\text{glycerol}} = 0.290$
 118. 1.0 m , 80% ionization; 2.0 m , 65% ionization; 4.0 m , 17% ionization
 126. 1.3 atm , 0.055 M

Chapter 15

16. (a) 2750 kJ (b) 58.1 g O_2
 18. $+98.9 \text{ kJ/mol rxn}$
 30. -584 kJ/mol
 32. $-1015.4 \text{ kJ/mol rxn}$
 34. $+197.6 \text{ kJ/mol rxn}$
 36. -289 kJ/mol rxn
 38. (a) $-124.0 \text{ kJ/mol rxn}$ (b) -1656 kJ/mol rxn
 (c) $+624.6 \text{ kJ/mol rxn}$
 40. $+46.36 \text{ kJ/g C}_3\text{H}_8$; $+44.27 \text{ kJ/g C}_8\text{H}_{18}$
 42. $+333 \text{ kJ}$ heat released
 44. sucrose: -5430 kJ/mol , -15.9 kJ/g , -3.79 kcal/g ;
 tristearin: -2900 kJ/mol , -3.3 kJ/g , -0.78 kcal/g
 48. (a) -121 kJ/mol rxn (b) -103 kJ/mol rxn
 50. -379 kJ/mol rxn
 52. -93 kJ/mol HCl ; -270 kJ/mol HF
 54. 329 kJ/mol
 56. 264 kJ/mol
 58. 288 kJ/mol
 60. $381 \text{ J/}^\circ\text{C}$
 62. $0.66 \text{ J/g}\cdot^\circ\text{C}$
 64. (a) $+2.1 \times 10^3 \text{ J}$ (b) $-1.0 \times 10^2 \text{ kJ/mol rxn}$
 66. $-41.9 \text{ kJ/g C}_6\text{H}_6(\text{l})$; $-3270 \text{ kJ/mol C}_6\text{H}_6(\text{l})$
 68. -23.1 kJ ; $-460. \text{ kJ/mol rxn}$
 70. $-2.08 \times 10^3 \text{ J/g C}_{10}\text{H}_{22}(\text{l})$; $-297 \text{ kJ/mol C}_{10}\text{H}_{22}(\text{l})$
 76. -336 J
 78. (a) by surroundings (b) by system (c) by surroundings
 80. (a) $+983 \text{ J}$ (b) 0 J
 86. (a) $\frac{1}{2}$ (b) $\frac{1}{4}$ (c) $1/1024$
 88. (a) 16 (b) 14 of 16 (c) $7/8$ (d) $1/8$
 104. (a) $-128.8 \text{ J/(mol rxn)}\cdot\text{K}$ (b) $-182 \text{ J/(mol rxn)}\cdot\text{K}$
 (c) $+148.6 \text{ J/(mol rxn)}\cdot\text{K}$
 108. $-432.8 \text{ J/(mol rxn)}\cdot\text{K}$
 110. $-53.42 \text{ kJ/mol rxn}$
 112. (a) $\Delta H^\circ = -71.75 \text{ kJ/mol rxn}$, $\Delta S^\circ = -268.0 \text{ J/(mol rxn)}\cdot\text{K}$, $\Delta G^\circ = +8.15 \text{ kJ/mol rxn}$
 (b) $\Delta H^\circ = +14.7 \text{ kJ/mol rxn}$, $\Delta S^\circ = +31.2 \text{ J/(mol rxn)}\cdot\text{K}$, $\Delta G^\circ = +5.4 \text{ kJ/mol rxn}$
 (c) $\Delta H^\circ = -367.6 \text{ kJ/mol rxn}$, $\Delta S^\circ = -11.62 \text{ J/(mol rxn)}\cdot\text{K}$, $\Delta G^\circ = -364.1 \text{ kJ/mol rxn}$
 116. (a) $\Delta H^\circ = -196.0 \text{ kJ/mol rxn}$, $\Delta G^\circ = -233.6 \text{ kJ/mol rxn}$, $\Delta S^\circ = +125.6 \text{ J/(mol rxn)}\cdot\text{K}$
 120. (a) spontaneous at all temperatures (b) spontaneous at $T > 839.3 \text{ K}$ (c) spontaneous at $T > 980.7 \text{ K}$
 (d) spontaneous at $T > 3000. \text{ K}$
 122. (a) 97°C
 126. $\Delta S^\circ = -247 \text{ J/(mol rxn)}\cdot\text{K}$, $\Delta H^\circ = -88.2 \text{ kJ/mol rxn}$, product favored at $T < 357 \text{ K}$
 128. (a) $-156 \text{ kJ/mol C}_6\text{H}_{12}(\text{l})$ (b) $-165 \text{ kJ/mol C}_6\text{H}_5\text{OH}(\text{s})$
 130. $q = +10700 \text{ J}$; $w = -788 \text{ J}$; $\Delta E = 9900 \text{ J}$
 132. (a) $2.88 \text{ kJ/}^\circ\text{C}$ (b) 23.82°C
 136. (a) sp. ht. = $0.13 \text{ J/g}\cdot^\circ\text{C}$, tungsten, W ($0.135 \text{ J/g}\cdot^\circ\text{C}$)
 (b) yes, sp. ht. = $0.26 \text{ J/g}\cdot^\circ\text{C}$, molybdenum, Mo
 142. 2.4 hr walking
 144. for Pb: sp. ht. = $0.13 \text{ J/g}\cdot^\circ\text{C}$; molar heat capacity, $27 \text{ J/mol}\cdot^\circ\text{C}$
 146. (a) 30.0 kJ/g (b) 7.17 kcal/g (c) 35.9 kcal

Unless otherwise noted, all content on this page is © Cengage Learning.

Chapter 16

10. O_2 : 1.50 M/min, NO : 1.20 M/min, H_2O : 1.80 M/min
 14. 1/2
 18. $\text{Rate} = (2.5 \times 10^{-2} \text{ M}^{-1} \cdot \text{min}^{-1})[\text{B}][\text{C}]$
 22. $\text{Rate} = (1.2 \times 10^2 \text{ M}^{-2} \cdot \text{s}^{-1})[\text{ClO}_2]^2[\text{OH}^-]$
 24. $\text{Rate} = (2.5 \times 10^{-3} \text{ M}^{-2} \cdot \text{s}^{-1})[\text{A}]^2[\text{B}]$
 26. $\text{Rate} = (20. \text{ M}^{-4} \cdot \text{s}^{-1})[\text{A}]^3[\text{B}]^2$
 28. 0.300 M/s, 1.20 M/s
 32. 5.29 s
 34. (a) $2.5 \times 10^6 \text{ s}$ (b) 41 days (c) 0.724 g Cs (d) 0.67 g
 36. (a) $2.4 \times 10^9 \text{ s}$ or 76 yrs (b) 0.59 M NO_2 , 54 g NO_2
 (c) 0.91 M NO reacted, 0.91 M NO produced
 38. 1680 s or 28.0 min
 40. $k_2/k_1 = 1.6$ for 90°C to 100°C , $k_2/k_1 = 2.2$ for 0°C to 10°C
 42. (a) zero order rxn, $\text{rate} = k = 0.00273 \text{ mM} \cdot \text{s}^{-1}$,
 $[\text{HI}] = [\text{HI}]_0 - akt = 5.46 \text{ mM} - (2)(0.00273 \text{ mM} \cdot \text{s}^{-1})t$
 (b) 2.18 mmol/L
 44. 8.4 s
 46. 462 d
 48. (a) $4.52 \times 10^{-29} \text{ s}^{-1}$ (b) $4.04 \times 10^{-10} \text{ s}^{-1}$
 54. 340 kJ/mol rxn
 56. 84 kJ/mol rxn
 58. 103 kJ/mol rxn
 60. (a) 270. kJ/mol (b) $7.7 \times 10^{-14} \text{ s}^{-1}$ (c) 730. K
 62. 2600 g $\text{CO}_2/\text{L} \cdot \text{min}$
 64. (a) 0.24 s^{-1} (b) 9°C
 66. (a) yes (b) no (c) no
 68. (a) $\text{Rate} = k[\text{A}]^2[\text{B}]^2$ (b) $\text{Rate} = k[\text{A}][\text{B}][\text{D}]$
 70. $\text{Rate} = k[\text{O}_3]^2/[\text{O}_2]$
 72. (a) N_2Cl (b) yes
 74. (b) yes
 78. (a) $8.7 \times 10^{-13} \text{ mol N}_2\text{O}_5$ (b) 19 s
 80. (a) $\text{Rate} = k[\text{Hb}][\text{CO}]$ (b) $0.280 \text{ L}/\mu\text{mol} \cdot \text{s}$
 (c) $0.252 \mu\text{mol}/\text{L} \cdot \text{s}$
 94. (1) 21 min, 42 min, 63 min (2) 21 min, 63 min, 150 min
 (3) same as (2)
 96. 64 kJ/mol
 100. $-200. \text{ kJ/mol rxn}$

Chapter 17

24. $K_c = 1.1 \times 10^{-5}$
 26. $K_c = 0.13$
 28. $K_c = 0.12$
 30. (a) $K_c' = 8.9 \times 10^5$ (b) $K_c'' = 1.3 \times 10^{-12}$
 (c) $K_c''' = 1.6 \times 10^{-24}$
 32. $K_c = 75$
 34. (a) $K_c = 4.49 \times 10^{-2}$ (b) $[\text{SbCl}_5] = 3.7 \times 10^{-3} \text{ M}$,
 $[\text{SbCl}_3] = [\text{Cl}_2] = 1.30 \times 10^{-2} \text{ M}$
 36. $K_c' = 6.502 \times 10^{-4}$
 42. (a) false (b) false (c) true (d) false
 44. 0.044 M
 46. 5.3 M
 48. 0.079 M
 50. 1 g (1 sig. fig.)
 52. $[\text{HI}] = 0.140 \text{ M}$, $[\text{H}_2] = [\text{I}_2] = 0.127 \text{ M}$
 64. (a) $K_c = 16$ (b) 0.35 M

66. (a) $K_c = 0.21$ (b) $[\text{A}] = 0.12 \text{ M}$, $[\text{B}] = [\text{C}] = 0.15 \text{ M}$
 (c) $[\text{A}] = 0.71 \text{ M}$, $[\text{B}] = [\text{C}] = 0.39 \text{ M}$
 68. (a) $[\text{N}_2\text{O}_4] = 0.0167 \text{ M}$, $[\text{NO}_2] = 9.90 \times 10^{-3} \text{ M}$
 (b) $[\text{N}_2\text{O}_4] = 1.05 \times 10^{-2} \text{ M}$, $[\text{NO}_2] = 7.82 \times 10^{-3} \text{ M}$
 (c) $[\text{N}_2\text{O}_4] = 0.0360 \text{ M}$, $[\text{NO}_2] = 0.0145 \text{ M}$
 72. $K_p = 1.6 \times 10^{-9}$
 74. $P_{\text{N}_2\text{O}_4} = 16 \text{ atm}$, $P_{\text{NO}_2} = 3.3 \text{ atm}$
 76. $K_p = 0.771$
 78. $K_c = 7.76$
 80. (a) 33.2%
 84. (a) $K_p = 1.1 \times 10^5$ (b) $K_p = 2.3 \times 10^2$
 (c) $K_p = 1.0 \times 10^5$
 86. $K_p = 7.0 \times 10^{24}$
 88. (a) -37.9 kJ/mol rxn at 25°C (b) $K_{p, 1073 \text{ K}} = 4.9 \times 10^{-4}$
 (c) $\Delta G^\circ = +68.0 \text{ kJ/mol rxn}$ at 800°C
 92. $P_{\text{CO}} = 0.685 \text{ atm}$, $P_{\text{CO}_2} = 0.315 \text{ atm}$
 96. At 400°C : $K_p = 8.3 \times 10^{-3}$, $K_c = 1.5 \times 10^{-4}$; at 800°C :
 $K_p = 16$, $K_c = 0.18$
 98. $K_p = 0.00432$
 112. $P_{\text{H}_2\text{O}} = 0.39$

Chapter 18

4. (a) 1.76 M NaCl (b) 0.770 M H_2SO_4 (c) $1.34 \times 10^{-3} \text{ M C}_6\text{H}_5\text{OH}$
 6. (a) $[\text{H}^+] = [\text{Br}^-] = 0.45 \text{ M}$ (b) $[\text{K}^+] = [\text{OH}^-] = 0.045 \text{ M}$ (c) $[\text{Ca}^{2+}] = 0.0112 \text{ M}$, $[\text{Cl}^-] = 0.0224 \text{ M}$
 8. (a) $[\text{K}^+] = [\text{OH}^-] = 0.0149 \text{ M}$ (b) $[\text{Ba}^{2+}] = 0.00585 \text{ M}$,
 $[\text{OH}^-] = 0.0117 \text{ M}$ (c) $[\text{Ca}^{2+}] = 0.0768 \text{ M}$, $[\text{NO}_3^-] = 0.154 \text{ M}$
 14. $2.2 \times 10^{-13} \text{ M}$; $4.76 \times 10^{-13} \text{ M}$; $8.55 \times 10^{-13} \text{ M}$;
 $1.00 \times 10^{-7} \text{ M}$
 16. 55.6 M H_2O ; $3.0 \times 10^{-23} \text{ H}_3\text{O}^+$ ions
 18. (a) 0.00, 14.00, acidic (b) 3.77, 10.23, acidic (c) 7.17,
 6.83, basic (d) 10.03, 3.97, basic
 20. $3.5 \times 10^{-8} \text{ M}$, $2.9 \times 10^{-7} \text{ M}$ at 25°C , $6.9 \times 10^{-7} \text{ M}$ at
 37°C
 22. (a) 0.70 (b) 1.30 (c) 2.19 (d) 10.99
 24. $3.0 \times 10^{-4} \text{ M}$
 26. (a) $\text{pH} = 12.93$ (b) $\text{pH} = 1.12$ (c) $\text{pH} = 13.18$
 32. triethylamine: $[\text{OH}^-] = 2.8 \times 10^{-3} \text{ M}$;
 trimethylamine: $[\text{OH}^-] = 1.1 \times 10^{-3} \text{ M}$
 34. (a) $\text{pH} = 6.82$ (b) neutral
 38. $\text{pH} = 3.096$, $K_a = 8.67 \times 10^{-6}$
 40. $K_a = 1.4 \times 10^{-3}$
 42. $[\text{C}_6\text{H}_5\text{COOH}] = 0.51 \text{ M}$, $[\text{H}_3\text{O}^+] = [\text{C}_6\text{H}_5\text{COO}^-] = 5.7 \times 10^{-3} \text{ M}$,
 $[\text{OH}^-] = 1.8 \times 10^{-12} \text{ M}$
 44. $\text{pH} = 1.78$
 46. $\text{pH} = 11.79$
 48. 4.9% ionized
 50. For weak acid #1: $\text{p}K_a = 4.14$; for weak acid #2:
 $\text{p}K_a = 9.38$
 52. $\text{p}K_b = 8.82$
 54. $K_b = 5.0 \times 10^{-4}$
 56. (a) $[\text{OH}^-] = 2.1 \times 10^{-3} \text{ M}$, 0.85% ionized,
 $\text{pH} = 11.32$ (b) $[\text{OH}^-] = 0.011 \text{ M}$, 4.4% ionized,
 $\text{pH} = 12.04$

58.

0.100 M H ₃ AsO ₄ Solution		0.100 M H ₃ PO ₄ Solution	
Species	Concentration (M)	Species	Concentration (M)
H ₃ AsO ₄	0.095	H ₃ PO ₄	0.076
H ₃ O ⁺	0.0050	H ₃ O ⁺	0.024
H ₂ AsO ₄ ⁻	0.0050	H ₂ PO ₄ ⁻	0.024
HAsO ₄ ²⁻	5.6×10^{-8}	HPO ₄ ²⁻	6.2×10^{-8}
OH ⁻	2.0×10^{-12}	OH ⁻	4.2×10^{-13}
AsO ₄ ³⁻	3.4×10^{-18}	PO ₄ ³⁻	9.3×10^{-19}

60. [H₃O⁺] = 0.16 M, [OH⁻] = 6.2×10^{-14} M, [HSeO₄⁻] = 0.14 M, [SeO₄²⁻] = 0.01 M
 62. pH = 1.52
 74. $K = 5.3 \times 10^{-10}$
 76. (a) $K_b = 2.2 \times 10^{-11}$ (b) $K_b = 4.0 \times 10^{-6}$ (c) $K_b = 5.6 \times 10^{-11}$
 78. (a) pH = 9.46 (b) pH = 11.39 (c) pH = 11.79
 80. (a) pH = 11.94 (b) pH = 8.20
 84. (a) $K_a = 1.4 \times 10^{-11}$ (b) $K_a = 6.7 \times 10^{-6}$ (c) $K_a = 1.4 \times 10^{-10}$
 86. (a) pH = 4.92 (b) pH = 5.64 (c) pH = 2.60
 92. (a) pH = 2.89, 0.87% hydrolysis (b) pH = 5.21, 8.2×10^{-3} % hydrolysis (c) pH = 6.17, 4.5×10^{-4} % hydrolysis
 94. [A⁻] = 6.7×10^{-4} M
 114. [H₃O⁺] = 2.9×10^{-3} M, pH = 2.54
 116. pH = 2.04
 118. +57 kJ/mol

Chapter 19

10. (a) pH = 3.27 (b) pH = 4.84
 12. (a) [OH⁻] = 3.0×10^{-5} M, pH = 9.48 (b) [OH⁻] = 6.8×10^{-6} M, pH = 8.83
 18. (a) [OH⁻] = 2.3×10^{-3} M, [H₃O⁺] = 4.3×10^{-12} M (b) [OH⁻] = 1.4×10^{-5} M, [H₃O⁺] = 7.4×10^{-10} M
 22. pH = 0.70
 24. pH decreases by 0.40 units (9.48 → 9.08)
 26. (a) pH = 9.31 (b) pH = 9.20 (c) pH = 1.00
 28. [BrCH₂COOH] = 4.1×10^{-2} M, [NaBrCH₂COO] = 0.26 M
 30. [C₂H₅NH₃⁺] = 0.0010 M
 32. [CH₃CH₂COOH] = 0.36 M
 34. 0.40 L NaOH, 0.60 L CH₃COOH
 36. (a) 0.625 M CH₃COOH (b) 0.150 M Ca²⁺ (c) 0.300 M CH₃COO⁻ (d) 3.8×10^{-5} M H⁺ (d) pH = 4.42
 38. 0.024 M ClCH₂COOH
 42. $K_a = 6 \times 10^{-9}$, pK_a = 8.2
 44. pH between 7.6 and 8
 46. pH = 8.40, phenolphthalein
 50. (a) pH = 0.8239 (b) pH = 0.9931 (c) pH = 1.250 (d) pH = 1.87 (e) pH = 4.0 (f) pH = 12.03
 52. (a) pH = 0.839 (b) pH = 1.217 (c) pH = 1.85 (d) pH = 12.265 (e) pH = 12.529 (f) pH = 12.618
 54. (a) pH = 3.22 (b) pH = 4.14 (c) pH = 4.57 (d) pH = 4.74 (halfway to the equivalence pt.) (e) pH = 5.11 (f) pH = 5.70 (g) pH = 6.02 (h) pH = 8.52 (at the equivalence pt.) (i) pH = 11.00 (j) pH = 11.60 (k) pH = 12.00

56. (a) pH = 2.74 (b) pH = 4.72 (c) pH = 4.97 (d) pH = 5.23 (e) pH = 5.51 (f) pH = 8.86 (g) pH = 11.54
 58. (a) pH = 8.90 (b) pH = 8.79 (c) pH = 8.69
 60. (b) 8.09 mL HCl (c) [(CH₃CH₂)₃N] = [H₃O⁺] = 1.7×10^{-6} M, [(CH₃CH₂)₃NH⁺] = [Cl⁻] = 0.157 M
 66. (a) pH = 2.00 (b) pH = 2.05 (c) pH = 2.22 (d) pH = 2.30 (e) pH = 3.00 (f) pH = 3.3 (g) pH = 5.62 (h) pH = 8.0 (i) pH = 8.73
 68. pH (NaCl) = 7.00, pH (NH₄Cl) = 4.76
 70. pH = 12.2
 74. (a) K_a for NH₄⁺ = 5.6×10^{-10} (b) K_b for ClO⁻ = 2.9×10^{-7} (c) basic
 80. 78.1% KHSO₄ by mass
 82. pH = 4.00
 84. 0.22 L HCl

Chapter 20

8. (a) $K_{sp} = 3.5 \times 10^{-5}$ (b) $K_{sp} = 7.7 \times 10^{-19}$ (c) $K_{sp} = 6.9 \times 10^{-15}$ (d) $K_{sp} = 1.01 \times 10^{-4}$
 12. $K_{sp} = 3.65 \times 10^{-11}$
 14. 6.9×10^{-3} g CaCO₃/L
 16. (a) 4.4×10^{-4} mol CuCl/L; 4.4×10^{-4} M Cu⁺; 4.4×10^{-4} M Cl⁻; 0.043 g CuCl/L (b) 6.5×10^{-7} mol Ba₃(PO₄)₂/L; 2.0×10^{-6} M Ba²⁺; 1.3×10^{-6} M PO₄³⁻; 3.9×10^{-4} g Ba₃(PO₄)₂/L (c) 2.1×10^{-3} mol PbF₂/L; 2.1×10^{-3} M Pb²⁺; 4.2×10^{-3} M F⁻; 0.51 g PbF₂/L (d) 2.5×10^{-7} mol Sr₃(PO₄)₂/L; 7.4×10^{-7} M Sr²⁺; 4.9×10^{-7} M PO₄³⁻; 1.1×10^{-4} g Sr₃(PO₄)₂/L
 18. 0.012 g BaSO₄
 20. 6.0×10^{-3} mol Ag₂SO₄/L of 0.12 M K₂SO₄
 28. precipitation does not occur
 30. precipitation does occur
 32. 0.013% Pb²⁺ in soln
 36. (a) AuBr (b) 1.5×10^{-6} M Au⁺; 99.985% Au⁺ precipitated (c) 9.4×10^{-11} M Au⁺; 6.2×10^{-7} M Ag⁺
 38. (a) PbCrO₄ (b) 3.6×10^{-13} M Pb²⁺ (c) 3.6×10^{-7} M Pb²⁺ (d) 0.050 M SO₄²⁻, 5.0×10^{-8} M CrO₄²⁻
 40. (a) (i) 2.0×10^{-11} M Zn²⁺ (ii) 1.0×10^{-8} M Zn²⁺ (iii) 3.6×10^{-6} M Zn²⁺ (b) (i) 1.7×10^{-7} M OH⁻ (ii) 1.0×10^{-8} M CO₃²⁻ (iii) 7.3×10^{-5} M CN⁻
 42. pH = 7.59
 44. 2.5×10^{-7} mol CaF₂/L
 46. a precipitate will form but not be seen
 48. (a) 6.7×10^{-8} mol Mg(OH)₂/L of 0.015 M NaOH (b) 1.6×10^{-5} mol Mg(OH)₂/L of 0.015 M MgCl₂
 50. precipitation will not occur
 52. (a) pH = 9.40 (b) 1.1×10^{-4} g Fe(OH)₂/100 mL
 54. 4.5×10^{-9} M Zn²⁺
 56. a precipitate will form but not be seen
 64. precipitation will not occur
 66. 99.955% I⁻ removed
 74. 6.0×10^{-6} M Cl⁻
 78. (a) 1.1×10^{-9} M (b) 0.017 M
 80. 0.6 g Ca²⁺/L
 82. 29% loss of MgCO₃

Chapter 21

18. (i) (a) 3 (b) 2 (c) 1
(ii) (a) 5.18×10^3 C (b) 1.63×10^3 C (c) 481 C
20. (a) 0.142 A (b) 1.12 g Cu
22. 0.242 g Rh
24. 0.873 C
26. 8.39 g Ag
28. (a) 0.0830 faradays (b) 8.01×10^3 C (c) 0.930 L_{STP} H₂
(d) pH = 13.220
30. 3.2 L Cl₂
32. 5.2 hr, 4.6 g Cu
34. (a) 0.0214 faradays (b) 2.31 g Ag (c) 5.18 g Fe(NO₃)₃
54. (a) +3.17 V (b) +0.62 V
56. 0.71 V
58. (a) yes (b) no
60. (a) yes (b) no
62. +1.78 V
64. (a) +1.08 V (b) -1.202 V
66. (a) no (b) yes (c) yes (d) no
68. (a) H₂ (b) Sn (c) Hg (d) Cl⁻ in base (e) H₂S (f) Ag
70. -1.207 V
72. (a) yes (b) +0.57 V
74. +5.80 V (K⁺/K with F₂/F⁻)
78. 0.0257
82. (a) 1.202 V (b) +1.16 V (c) 2.0 M
84. (a) +2.123 V (b) +2.143 V
86. $P_{F_2} = 2.2 \times 10^{-7}$ atm
88. +0.95 V
90. (a) +0.870 V (b) +0.148 V (c) +0.0527 V
92. +0.38 V
94. (a) $[Zn^{2+}]/[Ni^{2+}] = 2 \times 10^{17}$ (b) 1×10^{-17} M Ni²⁺;
2.00 M Zn²⁺
96. pH = 6.15
100. (a) $E_{cell}^0 = +0.736$ V; $\Delta G^0 = -355$ kJ/mol rxn;
 $K = 1 \times 10^{62}$
(b) $E_{cell}^0 = +0.368$ V; $\Delta G^0 = -35.5$ kJ/mol rxn;
 $K = 1.6 \times 10^6$
(c) $E_{cell}^0 = +1.833$ V; $\Delta G^0 = -1061$ kJ/mol rxn;
 $K = 8.6 \times 10^{185}$
102. (a) -0.25 V (b) -0.13 V (c) -0.065 V
104. $K = 2$ (1 sig. fig.)
116. (b) +2.33 V (c) +2.44 V (d) 0.0227 g Mg
118. 955 C
120. $[Mn^{2+}]/[Fe^{2+}] = 10^{-24}$
122. (a) +4 (b) +4 (c) 0 (d) Mg(s) (e) UF₄(s) (f) 10.2 A
(g) 0.0206 L HF(g) (h) yes, 2.45 g U
134. (a) $K_{sp} = 10^{-12}$ (b) $\Delta G^0 = +68$ kJ/mol rxn

Chapter 22

14. (a) 0.587 g/mol (b) 5.28×10^{10} kJ/mol of ⁶²Ni atoms
16. (a) 0.602 amu/atom (b) 0.602 g/mol (c) 9.00×10^{-11}
J/atom (d) 5.42×10^{10} kJ/mol (e) 8.79 MeV/nucleon
18. (a) 1.04×10^{11} kJ/mol of ¹²⁷I atoms (b) 6.83×10^{10}
kJ/mol of ⁸¹Br atoms (c) 2.89×10^{10} kJ/mol of
³⁵Cl atoms
54. 67.5 min (90.0%), 88.0 min (95.0%)
56. 7×10^{-16} s
58. 0.17 μg
60. 0.00236

62. 1.98×10^4 yr
66. (b) $\Delta E = -1.68 \times 10^9$ kJ/mol rxn
74. (b) $\Delta E = +1.15 \times 10^8$ kJ/mol rxn
76. 2.52×10^9 yr
78. fission = -1.40×10^{-13} J/amu ²³⁵U; fusion =
 -1.53×10^{-13} J/amu ²H

Chapter 23

34. 2 isomers

Chapter 24

20. $[C_6H_5NH_2] = 0.12$ M; $[C_6H_5NH_3^+] = [OH^-] =$
 7.1×10^{-6} M; $[H_3O^+] = 1.4 \times 10^{-9}$ M
28. pH = 10.78
48. 24 isomers
52. 9; A-A, A-B, A-C, B-A, B-B, B-C, C-A, C-B, C-C
72. pH (sodium benzoate) = 8.64; more acidic

Chapter 25

4. (a) 4 (b) 4
6. (a) ox. no. +3 (b) +3 (c) +2 (d) +2
20. (a) ox. no. +2 (b) +3 (c) +1 (d) +2 (e) +2 (f) +3
32. (a) 2 isomers (b) 2 isomers
36. (a) 2 isomers (b) 2 isomers (c) 2 optical isomers
(d) 3 isomers (e) 6 isomers
52. 8
58. $\Delta S_{rxn}^0 = -153.5$ J/(mol rxn)·K
60. pH = 10.43
64. (a) 2.2×10^{-6} mol Zn(OH)₂/L (b) 0.010 mol
Zn(OH)₂/L (c) $[Zn(OH)_4^{2-}] = 0.010$ M

Chapter 26

16. 39.997 g NaOH, 1.008 g H₂, 35.45 g Cl₂
40. 1.7×10^7 tons bauxite
46. (a) -15 kJ/mol rxn (b) +5 kJ/mol rxn (c) -25 J/
(mol rxn)·K
50. 21.0 g Cu
52. bornite (63.33% Cu)
54. 104 tons SO₂
56. 33.4 tons C (coke)

Chapter 27

32. (a) -201.4 kJ/mol rxn (b) -138.9 kJ/mol rxn
(c) -415.0 kJ/mol rxn
46. Be(OH)₂: $[OH^-] = 1.6 \times 10^{-7}$ M, pOH = 6.80,
Mg(OH)₂: $[OH^-] = 3.1 \times 10^{-4}$ M, pOH = 3.51,
Ca(OH)₂: $[OH^-] = 0.025$ M, pOH = 1.60, Sr(OH)₂:
 $[OH^-] = 0.086$ M, pOH = 1.06, Ba(OH)₂: $[OH^-] =$
0.22 M; pOH = 0.67
48. 22.61% Cr
56. 384 g Co₃O₄
58. $\Delta H_{rxn}^0 = -195.4$ kJ/mol Rb(s), $\Delta S_{rxn}^0 = 29.4$ J/K per
1 mol Rb(s), $\Delta G_{rxn}^0 = -204.0$ kJ/mol Rb(s)
60. 0.200 mol CO₂, Q = Li in Li₂CO₃

Chapter 28

8. 2.19 g XeF₆
42. 2.04 tons H₂SO₄
44. $K_c = 2.7$
52. (a) 0 (b) +1 (c) +4 (d) +5 (e) +3
82. -140 kJ/mol rxn
86. 2.2×10^{25} g Si
88. 1.92 Å

Index of Equations

Bold entries in parentheses are chapter and section numbers, followed by the page number.

Arrhenius equation (single temperature)

$$k = Ae^{-E_a/RT} \quad (16-8), 644$$

Arrhenius equation (two temperatures)

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (16-8), 645$$

Balmer–Rydberg equation

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (4-13), 139$$

Bohr energy

$$E = -\frac{1}{n^2} \left(\frac{h^2}{8\pi^2 m a_0^2} \right) = -\frac{2.180 \times 10^{-18} \text{ J}}{n^2} \quad (4-13), 142$$

Bohr radius

$$r = n^2 a_0 = n^2 \times 5.292 \times 10^{-11} \text{ m} \quad (4-13), 142$$

Boiling point elevation

$$\Delta T_b = K_b m \quad (14-11), 524$$

Bond order

$$\text{bond order} = \frac{\left(\begin{array}{c} \text{number of bonding} \\ \text{electrons} \end{array} \right) - \left(\begin{array}{c} \text{number of antibonding} \\ \text{electrons} \end{array} \right)}{2} \quad (9-3), 335$$

Boyle's Law

$$PV = \text{constant} \quad (\text{constant } n, T) \quad (12-4), 406$$

$$P_1 V_1 = P_2 V_2 \quad (\text{constant } n, T) \quad (12-4), 408$$

Bragg equation (x-ray diffraction)

$$n\lambda = 2d \sin \theta \quad (13-14), 476$$

Buffers

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} \quad (\text{for acid/salt buffer}) \quad (19-1), 753$$

and

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{conjugate acid}]}{[\text{base}]} \quad (\text{for base/salt buffer}) \quad (19-1), 756$$

Cell voltage, nonstandard conditions (Nernst equation)

$$E = E^0 - \frac{2.303 RT}{nF} \log Q \quad (21-19), 828$$

or

$$E = E^0 - \frac{0.0592}{n} \log Q$$

Charles's Law

$$V = kT \quad (\text{constant } n, P) \quad (12-5), 410$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{constant } n, P) \quad (12-5), 411$$

Clausius–Clapeyron equation

$$\ln \left(\frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (13-9), 467$$

Combined Gas Law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (\text{constant } n) \quad (12-7), 412$$

Concentrations:

Percent solute

$$\text{percent solute} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \quad (3-6), 98$$

Molarity, M			Enthalpy of reaction, ΔH_{rxn}^0 (gas-phase reaction, estimation from bond energies)	
molarity = $\frac{\text{number of moles of solute}}{\text{number of liters of solution}}$	(3-6), 99		$\Delta H_{\text{rxn}}^0 = \sum \text{B.E.}_{\text{reactants}} - \sum \text{B.E.}_{\text{products}}$	(15-9), 569
molarity = $\frac{\text{number of millimoles of solute}}{\text{number of milliliters of solution}}$	(11-1), 377		Enthalpy of reaction, ΔH_{rxn}^0 (Hess's Law), from enthalpies of formation	
Molarity, dilution $V_1M_1 = V_2M_2$ (for dilution only)	(3-7), 102		$\Delta H_{\text{rxn}}^0 = \sum n \Delta H_{\text{f products}}^0 - \sum n \Delta H_{\text{f reactants}}^0$	(15-8), 566
Molality, m			Enthalpy of reaction, ΔH_{rxn}^0 (Hess's Law), from enthalpies of related reactions	
molality = $\frac{\text{number of moles solute}}{\text{number of kilograms solvent}}$	(14-8), 516		$\Delta H_{\text{rxn}}^0 = \Delta H_{\text{a}}^0 + \Delta H_{\text{b}}^0 + \Delta H_{\text{c}}^0 + \dots$	(15-8), 564
Mole fraction, X			Enthalpy of solution, $\Delta H_{\text{solution}}$	
$X_{\text{A}} = \frac{\text{no. mol A}}{\text{total no. mol of all components}}$	(12-11), 422		$\Delta H_{\text{solution}} = (\text{heat of solvation}) - (\text{crystal lattice energy})$	(14-2), 509
Coulomb's law (electrostatic attraction)			Entropy of reaction, ΔS_{rxn}^0	
$F \propto \frac{q^+ q^-}{d^2}$	(5-3), 180		$\Delta S_{\text{rxn}}^0 = \sum n S_{\text{products}}^0 - \sum n S_{\text{reactants}}^0$	(15-14), 583
	(13-2), 453		Equilibrium constant—Gibbs free energy relationship	
Dalton's Law of partial pressures			$\Delta G_{\text{rxn}}^0 = -RT \ln K$	(17-12), 696
$P_{\text{total}} = P_{\text{A}} + P_{\text{B}} + P_{\text{C}} + \dots$ (constant V, T)	(12-11), 421		Equilibrium constant in terms of concentrations, K_{c}	
de Broglie equation			$K_{\text{c}} = \frac{\text{product concentrations}}{\text{reactant concentrations}} = \frac{[\text{C}]_{\text{eq}}^c [\text{D}]_{\text{eq}}^d}{[\text{A}]_{\text{eq}}^a [\text{B}]_{\text{eq}}^b}$	(17-2), 670
$\lambda = \frac{h}{mv}$	(4-14), 144		Equilibrium constant in terms of pressures, K_{p}	
Density, D			$K_{\text{p}} = \frac{(P_{\text{C}})^c (P_{\text{D}})^d}{(P_{\text{A}})^a (P_{\text{B}})^b}$	(17-9), 691
density = $\frac{\text{mass}}{\text{volume}}$ or $D = \frac{m}{V}$	(1-11), 26		Equilibrium constant, K_{a} , for weak acid HA	
Dilution			$K_{\text{a}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$	(18-4), 718
$V_1M_1 = V_2M_2$ (for dilution only)	(3-7), 102		Equilibrium constant, K_{b} , for weak base B	
Electrochemical potential vs. equilibrium constant			$K_{\text{b}} = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$	(18-4), 727
$nFE_{\text{cell}}^0 = RT \ln K$	(21-21), 835		Equilibrium constant, K_{sp} , for slightly soluble salt M_xX_y	
Electrochemical potential vs. standard free energy change			For $\text{M}_y^{x+} \text{X}_z^{y-} (\text{s}) \rightleftharpoons y\text{M}^{x+}(\text{aq}) + z\text{X}^{y-}(\text{aq})$,	
$\Delta G^0 = -nFE_{\text{cell}}^0$	(21-21), 835		$K_{\text{sp}} = [\text{M}^{x+}]^y [\text{X}^{y-}]^z$	(20-1), 781
Energy:			Equilibrium constant, relationship between K_{c} and K_{p}	
Matter—energy conversion			$K_{\text{p}} = K_{\text{c}}(RT)^{\Delta n}$ or $K_{\text{c}} = K_{\text{p}}(RT)^{-\Delta n}$	(17-10), 692
$E = mc^2$	(1-1), 5		$\Delta n = (n_{\text{gas prod}}) - (n_{\text{gas react}})$	
Photon energy				
$E = h\nu$ or $E = \frac{hc}{\lambda}$	(4-11), 137			
Kinetic energy				
$E_{\text{kinetic}} = \frac{1}{2}mv^2$	(15-1), 553			
Enthalpy change, ΔH				
$\Delta H = H_{\text{final}} - H_{\text{initial}}$ or				
$\Delta H = H_{\text{substances produced}} - H_{\text{substances consumed}}$	(15-3), 556			
$\Delta H = \Delta E + P \Delta V$ (constant T and P)	(15-11), 577			
$\Delta H = q_{\text{p}}$ (constant T and P)	(15-11), 577			

Equilibrium constant, thermodynamic

$$K = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b} \quad (17-12), 696$$

Equilibrium constants for conjugate acid–base pair

$$K_a K_b = K_w \quad (18-8), 734$$

First Law of Thermodynamics

$$\Delta E = q + w \quad (15-10), 571$$

Formal charge (for Group A elements)

$$\text{FC} = (\text{group number}) - [(\text{number of bonds}) + (\text{number of unshared } e^-)] \quad (7-7), 268$$

Formula weight (FW)

$$\text{FW} = \frac{\text{mass in grams}}{\text{no. of mol}} \quad (2-6), 58$$

Free energy change, ΔG

$$\Delta G = \Delta H - T \Delta S \quad (\text{constant } T \text{ and } P) \quad (15-16), 592$$

Free energy–equilibrium constant relationship

$$\Delta G_{\text{rxn}}^0 = -RT \ln K \quad (17-12), 696$$

Free energy of reaction, ΔG_{rxn}^0

$$\Delta G_{\text{rxn}}^0 = \sum n \Delta G_{\text{f products}}^0 - \sum n \Delta G_{\text{f reactants}}^0 \quad (1 \text{ atm and } 298 \text{ K only}) \quad (15-16), 592$$

Freezing point depression

$$\Delta T_f = K_f m \quad (14-12), 525$$

Frequency vs. wavelength

$$\lambda \nu = c \quad (4-11), 134$$

Half-life (first order, radioactive decay)

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \quad (16-4), 627 \quad (22-10), 863$$

Henderson–Hasselbalch equations

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} \quad (\text{for acid/salt buffer}) \quad (19-1), 753$$

and

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{conjugate acid}]}{[\text{base}]} \quad (\text{for base/salt buffer}) \quad (19-1), 756$$

Henry's Law (gas solubility)

$$C_{\text{gas}} = kP_{\text{gas}} \quad (14-7), 515$$

Hess's Law, enthalpy of reaction, ΔH_{rxn}^0 , from enthalpies of formation

$$\Delta H_{\text{rxn}}^0 = \sum n \Delta H_{\text{f products}}^0 - \sum n \Delta H_{\text{f reactants}}^0 \quad (15-8), 566$$

Hess's Law, enthalpy of reaction, ΔH_{rxn}^0 , from enthalpies of related reactions

$$\Delta H_{\text{rxn}}^0 = \Delta H_a^0 + \Delta H_b^0 + \Delta H_c^0 + \dots \quad (15-8), 564$$

Ideal gas equation

$$PV = nRT \quad (12-9), 415$$

Integrated rate equation, first order

$$\ln \left(\frac{[A]_0}{[A]} \right) = akt \quad (16-4), 627$$

Integrated rate equation, second order

$$\frac{1}{[A]} - \frac{1}{[A]_0} = akt \quad (16-4), 629$$

Integrated rate equation, zero order

$$[A] = [A]_0 - akt \quad (16-4), 631$$

Internal energy

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = E_{\text{products}} - E_{\text{reactants}} = q + w \quad (15-10), 571$$

$$\Delta E = q_v \quad (15-10), 573$$

Ion product for water, K_w

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14} \quad (\text{at } 25^\circ\text{C}) \quad (18-2), 711$$

 K_a , ionization constant for weak acid HA

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad (18-4), 718$$

 K_b , ionization constant for weak base B

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \quad (18-4), 727$$

 K_{sp} , solubility product constant for slightly soluble salt M_yX_z

$$\text{For } \text{M}_y^{x+}\text{X}_z^{y-}(\text{s}) \rightleftharpoons y\text{M}^{x+}(\text{aq}) + z\text{X}^{y-}(\text{aq}),$$

$$K_{\text{sp}} = [\text{M}^{x+}]^y [\text{X}^{y-}]^z \quad (20-1), 781$$

 K_w , ion product for water

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14} \quad (\text{at } 25^\circ\text{C}) \quad (18-2), 711$$

Kinetic energy, average molecular, $\overline{KE}$

$$\overline{KE} \propto T \quad (12-13), 429$$

Light, wavelength vs. frequency

$$\lambda \nu = c \quad (4-11), 134$$

Mass number (A)

$$\begin{aligned}\text{Mass number} &= \text{number of protons} + \text{number of neutrons} \\ &= \text{atomic number} + \text{neutron number (4-7), 123}\end{aligned}$$

Molality, *m*

$$\text{molality} = \frac{\text{number of moles solute}}{\text{number of kilograms solvent}} \quad (14-8), 516$$

Molarity, *M*

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \quad (3-6), 99$$

$$\text{molarity} = \frac{\text{number of millimoles of solute}}{\text{number of milliliters of solution}} \quad (11-1), 377$$

Mole fraction, *X*

$$X_A = \frac{\text{no. mol A}}{\text{total no. mol of all components}} \quad (12-11), 422$$

Mole fraction, *X*, in gas mixture

$$X_A = \frac{P_A}{P_{\text{total}}} \quad (12-11), 423$$

Moles, from mass

$$\text{mol} = \frac{\text{mass in grams}}{\text{formula weight}} \quad (2-6), 56$$

Moles, solute in solution

$$\text{moles solute} = \text{molarity} \times \text{L solution} \quad (3-6), 99$$

$$\text{millimoles solute} = \text{molarity} \times \text{mL solution} \quad (11-1), 377$$

Nernst equation

$$E = E^0 - \frac{2.303 RT}{nF} \log Q \quad (21-19), 828$$

or

$$E = E^0 - \frac{0.0592}{n} \log Q$$

Nuclear binding energy

$$BE = (\Delta m)c^2 \quad (22-3), 855$$

Nuclear mass deficiency

$$\begin{aligned}\Delta m &= (\text{sum of masses of all } e^-, p^+, \text{ and } n^0) \\ &\quad - (\text{actual mass of atom})\end{aligned} \quad (22-3), 854$$

Osmotic pressure

$$\pi = MRT \quad (14-15), 531$$

Percent solute

$$\text{percent solute} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \quad (3-6), 98$$

Percent yield

$$\text{percent yield} = \frac{\text{actual yield of product}}{\text{theoretical yield of product}} \times 100\% \quad (3-4), 95$$

pH

$$\begin{aligned}\text{pH} &= -\log [\text{H}_3\text{O}^+] & \text{or} & \quad [\text{H}_3\text{O}^+] = 10^{-\text{pH}} & (18-3), 713 \\ \text{pH} + \text{pOH} &= 14.00 & & \quad (\text{at } 25^\circ\text{C}) & (18-3), 714\end{aligned}$$

p*K_w*

$$\text{p}K_w = -\log K_w \quad (= 14.0 \text{ at } 25^\circ\text{C}) \quad (18-3), 713$$

pOH

$$\text{pOH} = -\log [\text{OH}^-] \quad \text{or} \quad [\text{OH}^-] = 10^{-\text{pOH}} \quad (18-3), 713$$

Quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (17-5), 679$$

Radioactive decay

$$\ln\left(\frac{A_0}{A}\right) = kt \quad \text{or} \quad \ln\left(\frac{N_0}{N}\right) = kt \quad (22-10), 863$$

Raoult's Law

$$P_{\text{solvent}} = X_{\text{solvent}} P^0_{\text{solvent}} \quad (14-9), 518$$

Raoult's Law, two volatile components

$$P_{\text{total}} = X_A P^0_A + X_B P^0_B \quad (14-9), 519$$

Rate equation, integrated, first order

$$\ln\left(\frac{[A]_0}{[A]}\right) = akt \quad (16-4), 627$$

Rate equation, integrated, second order

$$\frac{1}{[A]} - \frac{1}{[A]_0} = akt \quad (16-4), 629$$

Rate equation, integrated, zero order

$$[A] = [A]_0 - akt \quad (16-4), 631$$

Rate law expression

$$\text{rate} = k[A]^x[B]^y \dots \quad (16-3), 620$$

Rate of reaction

$$\begin{aligned}\text{rate of reaction} &= -\frac{1}{a}\left(\frac{\Delta[A]}{\Delta t}\right) = -\frac{1}{b}\left(\frac{\Delta[B]}{\Delta t}\right) \\ &= \frac{1}{c}\left(\frac{\Delta[C]}{\Delta t}\right) = \frac{1}{d}\left(\frac{\Delta[D]}{\Delta t}\right)\end{aligned} \quad (16-1), 615$$

Reaction quotient, Q

$$\text{For } aA + bB \rightleftharpoons cC + dD \quad (17-4), 674$$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \leftarrow \begin{array}{l} \text{not necessarily} \\ \text{equilibrium} \\ \text{concentrations} \end{array}$$

Second Law of Thermodynamics

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \quad (15-15), 590$$

Solubility product constant, K_{sp} , for slightly soluble salt M_xX_z

$$\begin{aligned} \text{For } M_y^{x+} X_z^{y-} (s) &\rightleftharpoons yM^{x+}(\text{aq}) + zX^{y-}(\text{aq}), \\ K_{\text{sp}} &= [M^{x+}]^y [X^{y-}]^z \end{aligned} \quad (20-1), 781$$

Specific gravity

$$\text{Sp. Gr} = \frac{D_{\text{substance}}}{D_{\text{water}}} \quad (1-11), 28$$

Specific heat

$$\text{specific heat} = \frac{(\text{amount of heat in J})}{(\text{mass of substance in g})(\text{temperature change in } ^\circ\text{C})} \quad (1-13), 32$$

Speed, average molecular, $\bar{u}$

$$\bar{u} \propto \sqrt{\frac{T}{\text{molecular weight}}} \quad (12-13), 429$$

Speed, gas molecule (root mean square)

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad (12-13), 433$$

Temperature conversions:

$$^\circ\text{C to K} \quad ^\circ\text{C} = \text{K} - 273.15^\circ \quad (1-12), 30$$

$$\text{K to } ^\circ\text{C} \quad \text{K} = ^\circ\text{C} + 273.15^\circ \quad (1-12), 30$$

$$^\circ\text{C to } ^\circ\text{F} \quad ^\circ\text{F} = \left(x^\circ\text{C} \times \frac{1.8^\circ\text{F}}{1.0^\circ\text{C}}\right) + 32^\circ\text{F} \quad (1-12), 31$$

$$^\circ\text{F to } ^\circ\text{C} \quad ^\circ\text{C} = \frac{1.0^\circ\text{C}}{1.8^\circ\text{F}} (x^\circ\text{F} - 32^\circ\text{F}) \quad (1-12), 31$$

van der Waals equation

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \quad (12-15), 437$$

van't Hoff equation

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (17-13), 699$$

van't Hoff factor, i

$$i = \frac{\Delta T_{\text{f(actual)}}}{\Delta T_{\text{f(if nonelectrolyte)}}} = \frac{K_{\text{f}} m_{\text{effective}}}{K_{\text{f}} m_{\text{stated}}} = \frac{m_{\text{effective}}}{m_{\text{stated}}} \quad (14-14), 529$$

or more generally, as

$$i = \frac{\text{colligative property}_{\text{actual}}}{\text{colligative property}_{\text{if nonelectrolyte}}}$$

Vapor pressure lowering

$$\begin{aligned} \Delta P_{\text{solvent}} &= P_{\text{solvent}}^0 - P_{\text{solvent}} \\ \Delta P_{\text{solvent}} &= X_{\text{solute}} P_{\text{solvent}}^0 \end{aligned} \quad (14-9), 518$$

Wavelength vs. frequency

$$\lambda\nu = c \quad (4-11), 134$$

Work

$$w = fd \quad (15-10), 571$$

Work, due to change in number of moles of gas (e.g., phase change or chemical reaction)

$$w = -(\Delta n)RT \quad (15-10), 574$$

Work, due to expansion

$$w = -P\Delta V \quad (15-10), 573$$

Glossary/Index

Glossary terms, printed in **boldface**, are defined here as well as in the text (location indicated by boldface page numbers) and in Key Terms. Page numbers followed by i indicate illustrations or their captions; page numbers followed by t indicate tables.

2-Deoxyribose The carbohydrate found in DNA, 978–981, 980–981f, **982**

α -Amino acid A compound containing both an amino group and a carboxylic acid group connected to a carbon atom (the α -carbon) that can have a variety of other organic groups attached. There are 22 common amino acids that are the building blocks for proteins and other biological molecules, **925–926**, **943**, 975, 976t

Absolute entropy (of a substance) The entropy of a substance relative to its entropy in a perfectly ordered crystalline form at 0 K (where its entropy is zero), **583**, **598**

Absolute zero The zero point on the absolute temperature scale, -273.15°C or 0 K; theoretically, the temperature at which molecular motion is a minimum, **410**, **438**

Absorption spectrum The spectrum associated with absorption of electromagnetic radiation by atoms (or other species) resulting from transitions from lower to higher electronic energy states, **139**, **140f**, **162**

Accuracy How closely a measured value agrees with the correct value, **35**

Acetic acid, **12t**, **733**, **756–757**, **961**, **961t**

Acetylene, **267**, **319**, **889f**, **905f**, **968**

Achiral Describes an object that *can* be superimposed with its mirror image, **956**, **982**

Acid A substance that produces H^+ (aq) ions in aqueous solution. Strong acids ionize completely or almost completely in dilute aqueous solution. Weak acids ionize only slightly, **208**, **240**, **349**, **363**. *see also*

Strong acid; Weak acid

amphoterism, **354–355**, **355f**

Arrhenius theory of, **349–350**

binary, **355–356**

Brønsted-Lowry theory, **350–353**

Lewis, **363–365**, **363–365f**

organic, **961–962**, **961–962t**, **968–969**

pH and pOH scales, **713–716**, **717f**

polyprotic, **729–732**, **731t**

preparation of, **365–366**, **365–366f**

properties of, **349**

strength of, **355–358**, **357t**

strong and weak, **209–211**, **211f**, **211t**, **212f**

ternary, **197**, **202**, **219–221**, **220t**, **240**, **357–358**, **366**, **367**

Acid (Arrhenius or Brønsted-Lowry) A substance that produces H^+ (aq) ions in aqueous solution. Strong acids ionize completely or almost completely in dilute aqueous solution; weak acids ionize only slightly, **367**

Acid anhydride A nonmetal oxide that reacts with water to form an acid, **195f**, **197**, **201**, **367**

Acid-base reaction. *see also* **Buffer solution; Coordination compound or complex; Neutralization reaction**

calculations summary, **771t**

indicators, **763–765**, **764f**, **766t**

molarity and, **376–380**

Acid-base titration The quantitative analysis of the amount or concentration of an acid or base in a sample by observing its reaction with a known amount or concentration of a base or acid, **382**, **393**

Acid halide. *see* **Acyl halide**

Acidic oxide. *see* **Acid anhydride**

Acidic salt A salt that contains an ionizable hydrogen atom; does not necessarily produce acidic solutions, **361–362**, **362f**, **367**

Actinides Elements 90 through 103 (after actinium), **201**

Activation energy, **639**, **645–647**

Active metal A metal that readily loses electrons to form cations, **240**

Activity (of a component of an ideal

mixture) A dimensionless quantity whose magnitude is equal to molar concentration in an ideal solution, equal to partial pressure (in atmospheres) in an ideal gas

mixture, and defined as 1 for pure solids or liquids, **700**

Activity series A listing of metals (and hydrogen) in order of decreasing activity, **229**, **240**

Actual yield The amount of a specified pure product actually obtained from a given reaction. Compare with Theoretical yield, **95**, **106**

Acyl group The group of atoms remaining after removal of an $-\text{OH}$ group of a carboxylic acid, **926**, **943**

Acyl halide A compound derived from a carboxylic acid by replacing the $-\text{OH}$ group with a halogen (X), usually $-\text{Cl}$;

general formula is $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}$; also known as an *Acid halide*, **926–927**, **943**, **968–969**

Addition polymer A polymer formed by an addition reaction, **938**, **943**

Addition reaction A reaction in which two atoms or groups of atoms are added to a molecule, one on each side of a double or triple bond. The number of groups attached to carbon *increases*, and the molecule becomes more nearly saturated, **935–937**, **943**

Adhesive force Force of attraction between a liquid and another surface, **460**, **494**

Adsorption Adhesion of species onto surfaces of particles, **535–537**, **538f**, **538t**, **542**

Air

composition of, **403**, **403t**

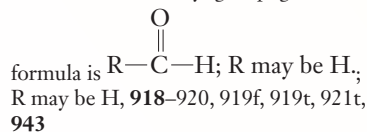
pollution and fossil fuels, **199–200**, **199f**, **200f**, **200t**

Alchemist in the Search of the Philosopher's Stone Discovers Phosphorus, The, **175**, **175f**

Alcohol A hydrocarbon derivative in which an H attached to a carbon atom not part of an aromatic ring has been replaced by an $-\text{OH}$ group, **913–918**, **913f**, **917f**, **917t**, **943**

formation of carboxylic acid derivatives, 968–969
 oxidation of, 965–966
 reactions, 961–962, 961–962t

Aldehyde A compound in which an alkyl or aryl group and a hydrogen atom are attached to a carbonyl group; general



reactions, 963–965, 965–966

Aldose A monosaccharide that contains an aldehyde group, **971, 982**

Aliphatic hydrogens Hydrocarbons that do not contain aromatic rings, **890, 943**

Alkali metals Elements of Group 1A in the periodic table, except hydrogen, **132, 162, 240, 1053**

compounds and their uses, 1041–1042, 1041f
 properties and occurrence, 1036–1037, 1037t
 reactions of, 1037–1040, 1040t
 reactions with halogens, 252–254
 reactions with nonmetals, 254

Alkaline cell A dry cell in which the electrolyte contains KOH, **838, 842**

Alkaline earth metals Group 2A elements in the periodic table, **132, 162, 240, 1053**
 compounds and their uses, 1043–1044, 1044f

properties and occurrence, 1042, 1042t
 reactions of, 1042–1043, 1043f, 1043t
 reactions with nonmetals, 255

Alkanes. *see* **Saturated hydrocarbons**

Alkenes Unsaturated hydrocarbons that contain a carbon-carbon double bond, 899–904, 899f, 901–902f, **943**

Alkylbenzene A compound containing an alkyl group bonded to a benzene ring, **907, 909–910, 909f, 943, 966–967**

Alkyl group A group of atoms derived from an alkane by the removal of one hydrogen atom, **895, 943**

Alkyl hydrogen sulfates, 935

Alkynes Unsaturated hydrocarbons that contain a carbon-carbon triple bond, 905–906, 905f, **943**

Allotropes Different structural forms of the same element, 44, **72, 487, 494**

Alloying Mixing of a metal with other substances (usually other metals) to modify its properties, **1030**

Alpha emission Radioactive decay in which an alpha particle is given off from the nucleus, **859–860, 882**

Alpha- (α -) particle A helium ion with a 2+ charge; an assembly of two protons and two neutrons, **162**

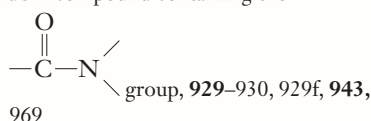
Alpha particle (α) A particle that consists of two protons and two neutrons; identical to a helium nucleus, 857, 858t, **859–860, 882**
 Aluminum, 85–86, 134, 560–561, 1024–1026, 1025f, 1045–1046, 1045t, 1047

Aluminum chloride, 364

Aluminum chlorohydrate, 362f

Aluminum hydroxide, 354–355

Amide A compound containing the



Amines Derivatives of ammonia in which one or more hydrogen atoms has been replaced by organic groups, 726–727, **742, 921–922, 922f, 943, 1073, 1080**
 reactions, 963

Amino group The $-\text{NR}_2$ group, where R can represent an H, alkyl, or aryl group, **943**

Ammine complexes Complex species that contain ammonia molecules bonded to metal ions, **993, 994t, 1010**

Ammonia, 192f, 390f, 792–793

ammine complexes, 993, 994t

buffer solutions, 755–756

Gay-Lussac's Law of Combining Volumes and, 428

neutralization with nitric acid, 361

pH of, 728

Ammonium chloride, 351f, 361f, 736, 754–755, 837

Ammonium ion, 300

Ammonium phosphate, 782

Ammonium sulfide, 207

Amorphous solid A noncrystalline solid with no well-defined, ordered structure, **475–477, 478f, 494**

Ampere Unit of electric current; 1 ampere equals 1 coulomb per second, **842**

Amphiprotism The ability of a substance to exhibit amphoterism by accepting or donating protons, **354, 367**

Amphoteric oxide An oxide that shows some acidic and some basic properties, 195f, **201**

Amphoterism The ability of a substance to react with both acids and bases, **201, 354–355, 355t, 367**

Amu. *see* **atomic mass unit (amu)**

Analytical chemistry, 3

Angstrom ($\text{\AA}$) 10^{-10} meter, 10^{-1} nm, or 100 pm, 23, 177, 178f, **201**

Angular A term used to describe the molecular geometry of a molecule that has two atoms bonded to a central atom and one or more lone pairs on the central atom (AB_2U or AB_2U_2); also called V-shaped or bent, **322**

Angular momentum quantum number (λ)

The quantum mechanical solution to a wave equation that designates the subshell, or set of orbitals (s, p, d, f), within a given main shell in which an electron resides, **148, 162**

Anhydrous Without water, **69–70, 72, 367**

Anion A negatively charged ion; that is, an ion in which the atom or group of atoms has more electrons than protons, **48, 72, 251, 280**

Anode In a cathode-ray tube, the positive electrode; the electrode at which oxidation occurs, **162, 805, 842**

Anthocyanins, 749f, 765f

Antibonding electrons Electrons in antibonding orbitals, 335, 338, **343**

Antibonding molecular orbital A molecular orbital higher in energy than any of the atomic orbitals from which it is derived; when populated with electrons, lends instability to a molecule or ion. Denoted with an asterisk (*) superscript on its symbol, 331–334, **343**

Aqueous solution A solution in which the solvent is water, **97, 106, 208–215. see also Titration**

acid-base reactions in, 358–361

electrolytes and extent of ionization, 208–209, 209f

properties, 349

reactions in, 215–217, 215t

reversible reactions, 211–212, 213t

solubility guidelines for compounds in, 213–215

strong and weak acids, 209–211, 211f, 211t, 212f

strong bases, insoluble bases, and weak bases, 212, 213t

Aromatic hydrocarbons Benzene and similar condensed ring compounds; contain delocalized rings of electrons, **890, 943**
 alkylbenzene, 907, 909–910, 909f
 benzene, 906–907, 907f

Arrhenius, S., 349

Arrhenius equation An equation that related the specific rate constant to activation energy and temperature, 643–647, 644–646f, **656**

Arrhenius theory, 349–350

Artificial transmutation An artificially induced nuclear reaction caused by bombardment of a nucleus with subatomic particles or small nuclei, 871–874, 872–873f, **882**

Artists' pigments, 924

Aryl group The group of atoms remaining after a hydrogen atom is removed from an aromatic system, **943**

Ascorbic acid, 709f

Associated ions Short-lived species formed by the collision of dissolved ions of opposite charge, **528, 542**

Atmosphere (atm) A unit of pressure; the pressure that will support a column of mercury 760 mm high at 0°C ; 760 torr., 404, 416, **438**

Atomic mass unit (amu) One-twelfth of the mass of an atom of the carbon-12 isotope; a unit used for stating atomic and formula weights, **51, 72, 162, 420**

Atomic number The integral number of protons in the nucleus; defines the identity of an element, **6, 35, 121–122, 132, 162, 240**

Atomic orbital The region or volume in space in which the probability of finding electrons is highest, **147, 148–153, 162, 297**

energy level diagrams, 333–334, 334f

Atomic radius The radius of an atom, 177–179, 184f, **201**

Atomic spectra, 138–144

Atomic weight Weighted average of the masses of the constituent isotopes of an

- element; the relative mass of atoms of different elements, **51, 72, 126, 128–129**
- Atom** The smallest particle of an element that maintains its chemical identity through all chemical and physical changes, **6, 35**
- atomic number, **121–122**
- atomic orbitals, **148–153**
- atomic spectra and the Bohr atom, **138–144**
- atomic weights, **126, 128–129**
- canal rays and protons, **119, 119f**
- discovery of, **5–6**
- discovery of electrons and, **164–165, 166f**
- donor, **994, 994t**
- electromagnetic radiation, **134–137**
- formal charges, **267–269**
- fundamental particles of, **163–164**
- Lewis dot formulas of, **250–251, 251t**
- mass number, **123–124**
- mass spectrometry and isotopic abundance, **124–125, 125f, 126f**
- moles of, **54**
- neutrons, **122–123**
- photoelectric effect, **138, 138f**
- quantum mechanical picture of, **146–147, 147f**
- quantum numbers, **147–148**
- Rutherford and nuclear atom, **120–121, 120–121f**
- wave nature of the electron and, **144–145**
- Aufbau (“building up”) Principle** A guide for predicting the order in which electrons fill subshells and shells in atoms, **153, 154f, 155f, 157, 162, 333**
- Autoionization** An ionization reaction between identical molecules, **353–354, 364, 367, 711–713, 725–726**
- Avogadro’s law** At the same temperature and pressure, equal volumes of all gases contain the same number of molecules, **414–415, 438**
- Avogadro’s number** 6.022×10^{23} units of a specified item. See Mole, **52, 55, 56, 72**
- metallic solids, **485–486**
- Baking soda, **362f, 762**
- Balancing chemical equations, **83–87, 376–380, 387**
- Ball-and-stick model, **45, 45f, 46f, 66f, 157f, 287f**
- alkanes, **891–893f**
- methane combustion, **83f**
- stereoisomers, **1002**
- Balmer-Rydberg equation** An empirical equation that relates wavelengths in the hydrogen emission spectrum to simple integers, **139–144, 162**
- Band** A series of very closely spaced, nearly continuous molecular orbitals that belong to the material as a whole, **494**
- Band gap (E_g)** An energy separation between an insulator’s highest filled electron energy band and the next higher-energy vacant band, **491, 491f, 492, 494**
- Band of stability** A band containing stable (nonradioactive) nuclides in a plot of number of neutrons *versus* number of protons (atomic number), **853, 854f, 859–860, 882**
- Band theory of metals** A theory that accounts for the bonding and properties of metallic solids, **489–493, 490–491f, 494**
- Bar** A unit of pressure; 1.00 bar is equal to 100. kPa (or 0.987 atm), **438**
- Barium, **144f, 811, 924, 1042, 1044**
- Barium hydroxide, **100–101, 195, 213t, 554f**
- Barium sulfate, **780–781, 781f, 782**
- Barometer** A device for measuring atmospheric pressure (see Figures 12-1 and 12-2). The liquid is usually mercury, **403, 404f, 405f, 438**
- Bartlett, Neil, **1059**
- Base** A substance that produces OH^- (aq) ions in aqueous solution. Strong bases are soluble in water and are completely dissociated. weak bases ionize only slightly, **240, 349, 363. see also Coordination compound or complex; Strong base; Weak base**
- amphoterism, **354–355, 355f**
- Arrhenius theory of, **349–350**
- Brønsted-Lowry theory, **350–353**
- Lewis, **363–365, 363–365f**
- in nucleic acid, **980**
- organi, **963**
- pH and pOH scales, **713–716, 717f**
- properties of protic, **349**
- strong, insoluble and weak, **212, 213t**
- Base (Arrhenius)** A substance that produces OH^- (aq) ions in aqueous solution. Strong bases are soluble in water and are completely dissociated. Weak bases ionize only slightly, **367**
- Base-pairing** The complementary hydrogen bonding of cytosine with guanine and of adenine with thymine (in DNA) or with uracil (in RNA), **982**
- Basic anhydride** A metal oxide that reacts with water to form a base, **195, 201, 367**
- Basic oxide. *see* **Basic anhydride**
- Basic salt** A salt containing a basic OH group, **361–362, 362f, 367**
- Battery** A voltaic cell (or a set of voltaic cells coupled together) that has been designed for practical use, **842**
- alkaline cell, **838**
- dry cell, **837–838**
- lead storage, **838–840, 839f**
- nickel-cadmium, **840**
- Becquerel, Henri, **852, 861**
- Benzene, **12t, 329f, 341–342, 906–907, 907f**
- Bernoulli, Daniel, **428, 431**
- Beryllium, **159, 295, 296–297, 1042–1043, 1044f**
- Beryllium chloride, **270**
- Beta emission** Radioactive decay in which an electron is ejected from the nucleus to convert a neutron into a proton, **859, 882**
- Beta particle (β)** An electron emitted from the nucleus when a neutron decays to a proton and an electron, **859, 882**
- Bethe, Hans, **1006**
- Binary acid** A binary compound in which H is bonded to a nonmetal in Group 7A or a nonmetal other than oxygen in Group 6A, **240, 355–356**
- Binary compound** A compound consisting of two elements; may be ionic or molecular, **217–218, 219t, 240, 280**
- Binary ionic compounds, **217–218, 219t, 255–256, 256t**
- Binding energy (nuclear binding energy)** The energy equivalent ($E = mc^2$) of the mass deficiency of an atom, **882**
- nuclear stability and, **854–857, 857f**
- Biochemistry, **3**
- Biodegradability** The ability of a substance to be broken down into simpler substances by bacteria, **541, 542**
- Biological catalysts, **653, 653f**
- Biopolymer** Polymers found in biological systems, **970–971, 982**
- carbohydrates, **971–974, 971–974f, 972–973t**
- nucleic acid, **978–981, 980–981f**
- Bohr, Niels, **139, 143f**
- Bohr atom, **138–144**
- Boiling point** The temperature at which the vapor pressure of a liquid is equal to the external pressure; also the condensation point, **464, 464–465, 468, 469, 494**
- diagram, **522, 522f**
- hydrides, **455, 455f**
- Boiling point elevation** The increase in the boiling point of a solvent caused by dissolution of a nonvolatile solute, **523–524, 523f, 524t, 542**
- determination of molecular weight by, **526–527**
- Boiling point elevation constant, K_b** A constant that corresponds to the change (increase) in boiling point produced by a one-molal ideal solution of a nonvolatile nonelectrolyte, **524, 542**
- Bombardment
- neutron, **873–874**
- nuclear fission and, **874–876, 875–876f**
- with positive ions, **872–873, 872–873f**
- Bomb calorimeter** A device used to measure the heat transfer between system and surroundings at constant volume, **575–576, 577f, 598**
- Bond dissociation energy** The stabilization of a bonded pair of atoms compared to the same atoms when separated; the energy required to break the bonding between a pair of atoms; also known as *bond energy*, **259–260, 260t, 280**
- Bond energy** The amount of energy necessary to break one mole of bonds in a gaseous substance to form gaseous products at the same temperature and pressure, **335, 343, 568–571, 569t, 570f, 598. see also Bond dissociation energy**
- Bonding electrons** Electrons in bonding orbitals, **267, 275, 297, 306, 335, 343**
- Bonding molecular orbital** A molecular orbital lower in energy than any of the atomic orbitals from which it is derived; when populated with electrons, lends stability to a molecule or ion, **331, 343**
- Bonding pair** A pair of electrons involved in a covalent bond; also known as *shared pair*, **261, 280**

Bond length The distance between the centers (nuclei) of two bonded atoms, **259–260**, **260t**, **280**

Bond order Half the number of electrons in bonding orbitals minus half the number of electrons in antibonding orbitals, **335**, **343**

Bond stability, **335**

Boron, **126t**, **297–298**

molecule, **336**

Boron trichloride, **271**, **363**, **363f**

Boyle, Robert, **349**, **403**, **405**

Boyle's Law At constant temperature, the volume occupied by a given mass of a gas is inversely proportional to the applied pressure, **405–410**, **408f**, **430**, **438**

Combined Gas Law equation, **412–413**

Bragg, Lawrence, **476**

Bragg, William, **476**

Bragg equation, **476**

Breeder reactor A fission reactor that produces more fissionable material than it consumes, **878**, **882**

Bromine, **10f**, **12t**, **642–643**, **1062**

Brønsted–Lowry acid A proton donor, **367**, **982**

reactions, **960–963**, **961–962t**

Brønsted–Lowry base A proton acceptor, **367**

reactions, **960–963**, **961–962t**

Brønsted–Lowry theory The description of an acid as a proton donor and a base as a proton acceptor; also known as the *Brønsted theory*, **350–353**, **351f**, **352f**, **367**

autoionization of water, **353–354**

Buffer solution A solution that resists changes in pH when strong acids or strong bases are added. A buffer solution contains an acid and its conjugate base, so it can react with added base or acid. Common buffer solutions contain either (1) a weak acid and a soluble ionic salt of the weak acid, *or* (2) a weak base and a soluble ionic salt of the weak base, **750–756**, **752t**, **772**

buffering action, **756–759**

complex, **763**

pH, **759–760**

preparation, **759–763**

prepared by partial neutralization, **762–763**

Buret A piece of volumetric glassware, usually graduated in 0.1-ml intervals, that is used in titrations to deliver solutions in a quantitative (dropwise) manner, **380**, **381f**, **384f**, **393**

Butane, **84–85**, **960**, **960f**

Butter, **930**

Caffeine, **249**

Calcium, **1044**

Calcium carbonate, **16f**, **236**, **779f**

Calcium chloride, **348**, **505f**

Calcium phosphate, **235**

Calcium sulfate, **70–71**

Calculations in acid–base reactions

molarity, **376–380**

redox titrations, **390–393**

titration, **382–386**

Calorie Defined as exactly 4.184 joules.

Originally defined as the amount of heat

required to raise the temperature of one gram of water from 14.5°C to 15.5°C, **31**, **35**

Calorimeter A device used to measure the heat transfer that accompanies a physical or chemical change, **556–558**, **557f**, **598**

bomb, **575–576**, **577f**

Canal ray A stream of positively charged particles (cations) that moves toward the negative electrode in a cathode-ray tube; observed to pass through canals (holes) in the negative electrode, **119**, **162**

Cancer, **868–870**

Capillary action The drawing of a liquid up the inside of a small-bore tube when adhesive forces exceed cohesive forces, or the depression of the surface of the liquid when cohesive forces exceed adhesive forces, **460**, **461f**, **494**

Capsaicin, **953**

Carbohydrate A biopolymer made up of saccharide units, **971–974**, **971–974f**, **972–973t**, **982**

Carbonate ion, **341**, **342f**

Carbonates, **762**

Carbon dioxide, **7f**

greenhouse effect and, **406–407**

Carbonic acid, **238**, **348**

Carbon monoxide, **641–642**

Carbonyl group The $\begin{array}{c} \text{O} \\ || \\ -\text{C}- \end{array}$ group, **943**, **966**

Carboxylic acid A compound containing the

$\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{O}-\text{H} \end{array}$ carboxyl group, **922–926**, **923f**, **923t**, **926f**, **926t**, **943**

derivatives, **926–930**, **927f**, **928t**, **929f**, **968–969**

Carotene, **902f**

Cast iron The brittle iron obtained when the pig iron from the blast furnace is remelted, run into molds, and cooled; contains much iron carbide, Fe_3C , **1027**, **1030**

Catalyst A substance that increases the rate at which a reaction occurs. It is regenerated during the course of the reaction and can then interact with more reactants to convert them into products, **201**, **647–653**, **647–653f**, **656**

chemical equilibrium and, **684–686**

enzymes as biological, **653**, **653f**

heterogeneous, **649–653**, **650–652f**

homogeneous, **648–649**

Cathode In a cathode-ray tube, the negative electrode; the electrode at which reduction occurs, **162**, **805**, **842**

Cathode protection Protection of a metal against corrosion by making it a cathode (attaching it to a sacrificial anode of a more easily oxidized metal), **842**

Cathode ray The beam of electrons going from the negative electrode toward the positive electrode in a cathode-ray tube, **162**

Cathode-ray tube A closed glass tube containing a gas under low pressure, with electrodes near the ends and a

luminescent screen at the end near the positive electrode; produces cathode rays when high voltage is applied, **117**, **119f**, **162**, **165f**

Cation A positively charged ion; that is, an ion in which the atom or group of atoms has fewer electrons than protons, **48**, **72**, **251**, **280**

salts that contain small, highly charged, **740–741**, **740f**

Cell membranes and transport, **979**

Cell potential Potential difference, E_{cell} between reduction and oxidation half-cells; may be at *nonstandard* conditions, **842**

Cellulose, **973**, **973f**

Celsius, Anders, **29**

Celsius scale, **29–31**, **30f**

Central atom An atom in a molecule or polyatomic ion that is bonded to more than one other atom; the atom or ion to which the ligands are bonded in a complex species, **290**, **322**, **996**, **1010**

Cesium, **133**

Chadwick, James, **119**, **122**

Chain initiation step The first step in a chain reaction; produces reactive species (such as radicals) that then propagate the reaction, **1063**, **1080**

Chain propagation step An intermediate step in a chain reaction; in such a step one or more reactive species is consumed, and another reactive species is produced, **1063**, **1080**

Chain reaction A reaction in which reactive species, such as radicals, are produced in more than one step. Consists of an initiation step, one or more propagation steps, and one or more termination steps, **875**, **882**, **1063**, **1080**

Chain termination step The combination of reactive species (such as radicals) that terminates the chain reaction, **1063**, **1080**

Charge (in metallurgy) A sample of crushed ore as it is admitted to a furnace for smelting, **1030**

Charge density of an ion The ionic charge divided by the ionic radius in Angstroms, **510**, **542**

Charles, Jacques, **403**, **410**, **410f**

Charles' Law At constant pressure, the volume occupied by a definite mass of a gas is directly proportional to its absolute temperature, **410–412**, **411f**, **431**, **431f**, **438**

Combined Gas Law equation, **412–413**

Chelate A ligand that utilizes two or more connected donor atoms in bonding to metals, **994–995**, **1010**

Chemical bonds Attractive forces that hold atoms together in elements and compounds, **250**, **280**. *see also* **Bond energy**

continuous range of, **279**

in solids, **481–482f**, **481–489**, **481t**, **486–489f**

Chemical change A change in which one or more new substances are formed, also known as *chemical reaction* or just *reaction*, **12–13**, **13f**, **35**

Chemical communication, 964

Chemical equation Description of a chemical reaction by placing the formulas of reactants on the left and the formulas of products on the right of an arrow. A chemical equation must be balanced, that is, it must have the same number of each kind of atom on both sides, **82–87**, **106**

balancing, 83–87

calculations based on, 88–91

Chemical equilibrium A state of dynamic balance in which the rates of forward and reverse reactions are equal; there is no net change in concentrations of reactants or products while a system is at equilibrium, **668–670**, **669–670f**, **700**. *see also* **Equilibrium**

addition of catalyst and, 684–686

disturbing a system at, 679–686, 688–691

equilibrium constant, 670–673

Haber process and, 686–688, 687f, 687t

heterogeneous equilibria and, 694–695

partial pressures and, 691–692

reaction quotient, 674–676

relationship between free energy change and equilibrium constant, 695–698, 697f

relationship between K_p and K_c , 692–694

temperature changes and, 684, 699

uses of equilibrium constant and, 676–679

variation of K_c with the form of the balanced equation, 673–674

volume, pressure, and, 682–684

Chemical formula Combination of element symbols that indicates the chemical composition of a substance, **44–47**, **44–47f**, **45t**, **72**

ionic compounds, 49–51

other interpretations of, 67–71

Chemical kinetics The study of rates and mechanisms of chemical reactions and of the factors on which they depend, **612**, **656**. *see also* **Kinetic energy**

Arrhenius equation, 643–647, 644–646f

catalysts, 647–653, 647–653f

collision theory, 638, 638f

integrated rate equation, 627–637, 630f, 632t

nature of reactants and, 619

rate-law expression, 619–626, 632t

transition state theory, 638–640, 639–640f

Chemical periodicity The variation in properties of elements with their positions in the periodic table, 129–130, **162**, **173**

Chemical properties. *see* **properties**

Chemical reaction. *see also* **Rate of reaction**
combination reaction, 225–226, 225t, 239t, 240

decomposition reaction, 16f, 226–227, 227f, 239t, 240

displacement reaction, 227–228, 227–228f, 227–232, 229t, 231f, 239t, 240

gas-formation reaction, 237–238, 239t, 240

metathesis reaction, 232–237, 233t, 236f, 239t, 240

oxidation-reduction, 222–225, 239t, 240

standard molar entropy and, 585

Chemistry

defined, 2

measurements in, 19, 19t

molecular view of matter in, 5–9

roles of, 3

Chiral Describes an object that *cannot* be superimposed with its mirror image, **956**, **982**

Chlorine, 10f, 16f, 126t, 390f, 1061

Chlorofluorocarbons, 654–655

Chlorophyll, 991

Chocolate, 249

Chromium, 67–68, 822, 1039

Chromium oxides, 1050–1051, 1051t

cis-trans isomerism, 1000–1003, 1002f. *see*

Geometric isomerism

Citric acid, 210f, 347f, 349, 709f, 717, 727f, 729f, 762, 926t

Clausius-Clapeyron equation An equation that relates the change in vapor pressure of a liquid to the change in its temperature and its molar heat of vaporization, **467**, **494**

Clausius, Rudolf, 428

Climate change, 406–407

Cloud chamber A device for observing the paths of speeding particles as vapor molecules condense on the ionized air molecules in their tracks, **861**, **862f**, **882**

Cobalt, 8f, 1039

Cobalt-60, 864

Coffee, 249, 506, 915f

Cohesive forces All the forces of attraction among particles of a liquid, 460, 463, **494**

Colligative properties Physical properties of solutions that depend on the number, but not the kind, of solute particles present, **517**, **542**

boiling point elevation, 523–524, 524t

determination of molecular weight by freezing point depression or boiling point elevation, 526–527

dissociation of electrolytes and, 527–531, 528f, 529t

fractional distillation, 522–523, 522–523f

freezing point depression, 525–526

lowering of vapor pressure and Raoult's Law, 518–519f, 518–521, 521f

osmotic pressure, 531–535, 532f

Collision theory A theory of reaction rates that states that effective collisions between reactant molecules must take place for reaction to occur, **638**, **638f**, **656**

Colloid A heterogeneous mixture in which solute-like particles do not settle out; also known as a *colloidal dispersion*, **535**, **542**

adsorption phenomenon, 535–537, 538f, 538t

hydrophilic, 539

hydrophobic, 539–541

Tyndall effect, 535

Color. *see* **Complementary color**; **Spectral color**

Combination reaction Reaction in which two substances (elements or compounds) combine to form one compound, **225–226**, **225t**, **239t**, **240**

Combined Gas Law equation, 412–413

Combustion analysis, 63–65, 63f

Combustion reaction The rapid oxidation-reduction reaction of an oxidizable substance with oxygen in a highly

exothermic reaction, usually with a visible flame, 190, 199–200, 199f, 200f, 200t, **201**, 559–560

butane, 84–85

dimethyl ether, 84

methane, 81f, 82–83, 83f

organic compounds, 967–968, 967t

Combustion train, 63–65, 63f

Common ion effect Suppression of ionization of a weak electrolyte by the presence in the same solution of a strong electrolyte by containing one of the same ions as the weak electrolyte, **750–756**, 752t, **772**, 785–786, 789, **797**

Complementary color The color associated with the wavelengths of light that are not absorbed—that is, the color transmitted or reflected, **1008–1009**, 1008–1009t, **1010**

Complex ions Ions resulting from the formation of coordinate covalent bonds between simple cations and other ions or molecules (ligands), **797**. *see also*

Coordination compound or complex formation, 796

Composition stoichiometry Describes the quantitative (mass) relationships among elements in compounds, 44, **72**

Compound A substance composed of two or more elements in fixed proportions. Compounds can be decomposed into their constituent elements, **15**, **35**. *see also* inorganic compounds; organic compounds
combination reactions, 225–226, 225t
common, 45t

composition of, 67–71

containing double bonds, 317–319, 320–321f

containing triple bonds, **319–320**, 319f, 320f

decomposition reactions, 226–227, 227f

displacement reactions, 227–228, 227–228f

electron-deficient, 271

formulas of, **60–61**

Concentration The amount of solute per unit volume or mass of solvent or of solution, **97–101**, **106**

cells, 834

disturbing a system at equilibrium and, 679–681

effect on electrode potentials, 827–836, 833–834f

equilibrium, 678–679

integrated rate equation, 627–637

of reactants and reaction rate, 619–626

using electrochemical cells to determine, 832–834, 833f

Concentration cell A voltaic cell in which the two half-cells are composed of the same species by contain different ion concentration, **834**, **842**

Condensation The process by which a gas or vapor becomes a liquid; liquefaction, 450, 461, **466**, **494**

Condensation polymer A polymer that is formed by a condensation reaction, **940–942**, 941–942f, **943**

Condensation reaction A reaction in which a small molecule, such as water or hydrogen chloride, is eliminated and two molecules are joined, **940–942**, 941–942f, **943**

Unless otherwise noted, all content on this page is © Cengage Learning.

- Condensed phases** The liquid and solid phases; phases in which particles interact strongly, **450, 494**
- Condensed states** The solid and liquid states, **402, 438**
- Conduction band** A partially filled band or a band of vacant energy levels just higher in energy than a filled band; a band within which, or into which, electrons must be promoted to allow electrical conduction to occur in a solid, **490, 494**
- Conformation** One specific geometry of a molecule. The conformations of a compound differ from one another only by rotation about single bonds, **959–960, 959–960f, 982**
- Conjugate acid-base pair** In Brønsted-Lowry terminology, a reactant and product that differ by a proton, H^+ , **351, 367**
- Conjugated double bonds** Double bonds that are separated from each other by one single bond, as in $C=C-C=C$, **902, 943**
- Constitutional isomers** Compounds that contain the same numbers of the same kinds of atoms but that differ in the order in which their atoms are bonded together; also known as *structural isomers*, **893, 943, 954–955, 982, 999–1000**
- Contact process** An industrial process by which sulfur trioxide and sulfuric acid are produced from sulfur dioxide, **1080**
- Continuous spectrum** A spectrum that contains all wavelengths in a specified region of the electromagnetic spectrum, **134t, 135, 162**
- Control rods** Rods of materials such as cadmium or boron steel that act as neutron absorbers (not merely moderators), used in nuclear reactors to control neutron fluxes and therefore rates of fission, **877, 882**
- Cooling system, light water reactor, **877–878**
- Coordinate covalent bond** A covalent bond in which both shared electrons are furnished by the same species; the bond between a Lewis acid and a Lewis base, **363, 367, 990. see also Dative bond**
- Coordination compound or complex** A compound containing dative bonds between electron pair donors (ligands) and a metal; also known as *complex ion*, **990–993, 991–992t, 991f, 1010**
- ammine complexes, **993, 994t**
- bonding in, **1006–1009, 1006f, 1008–1009t**
- important terms, **994–996, 994–996t**
- isomerism in, **998–1005, 1002f, 1004–1005f**
- nomenclature, **996–997, 997t**
- structures, **998**
- Coordination isomers** Isomers involving exchange of ligands between a complex cation and a complex anion of the same coordination compound, **998–999, 1010**
- stereoisomers, **1000–1005, 1002f, 1004–1005f**
- structural, **999–1000**
- Coordination number** In describing crystals, the number of nearest neighbors of an atom or ion, **482, 494, 996, 997t, 1010**
- Coordination sphere** The metal ion and its coordinated ligands, but not any uncoordinated counterions, **996, 1010**
- Copolymer** A polymer formed from two different compounds (monomers), **939, 943**
- Copper, **8f, 811, 822, 1028–1029, 1030f**
- deficiency, **1039**
- SHE cell, **818–819, 819f**
- Copper-silver cell, **815–816, 816f**
- Copper sulfate, **69–70, 558**
- Corrosion** Oxidation of metals in the presence of air and moisture, **825–826f, 825–827, 842**
- Coulomb (C)** Unit of electric charge; the amount of charge that passes a given point when 1 ampere of electric current flows for 1 second, **117, 842**
- Coulomb's Law, **180, 215, 253, 453**
- Coulometry** The use of electrochemical cells to relate the amount of reactant or product to the amount of current passed through the cell, **808–811, 809t, 842**
- Covalent bond** A chemical bond formed by the sharing of one or more electron pairs between two atoms, **250, 279, 280, 488–489, 489f**
- formation of, **258–259**
- hybridization of carbon in, **889, 889t**
- lengths and energies, **259–260, 260t**
- polar and nonpolar, **276–278**
- Covalent compound** A compound containing predominantly covalent bonds, **250, 280**
- Critical mass** The minimum mass of a particular fissionable nuclide, in a given volume, that is required to sustain a nuclear chain reaction, **875, 882**
- Critical point** The combination of critical temperature and critical pressure of a substance, **474, 494**
- Critical pressure** The pressure required to liquefy a gas (vapor) at its critical temperature, **494**
- Critical temperature** The temperature above which a gas cannot be liquefied; the temperature above which a substance cannot exhibit distinct gas and liquid phases, **474, 494**
- Crystal field splitting energy** The energy separation between sets of d orbitals in a crystal field. In an octahedral complex, this is denoted by Δ_{oct} and is the energy separation between the e_g and t_{2g} sets of orbitals, **1007, 1010**
- Crystal field theory** A theory of bonding in transition metal complexes in which ligands and metal ions are treated as point charges; a purely ionic model. Ligand point charges represent the crystal (electric) field perturbing the metal's d orbitals that contain nonbonding electrons, **1006–1008, 1006f, 1008t, 1010**
- Crystal lattice energy, **253, 508**
- Crystal lattice** The pattern of arrangement of particles in a crystal, **494**
- structures, **478–480, 478t, 479–480f**
- Crystal lattice energy** The energy change when one mole of formula units of a crystalline solid is formed from its ions, atoms, or molecules in the gas phase; always negative, **542**
- Crystalline solids, **475–477, 478f**
- Crystallization, **451, 513**
- Curie, Marie, **852, 853f**
- Curie, Pierre, **852**
- Cycloalkanes** Cyclic saturated hydrocarbons, **890, 895, 895f, 943**
- Cyclotron** A device for accelerating charge particles along a spiral path, **872–873, 872–873f, 882**
- Dalton's Atomic Theory, **6, 116**
- Dalton, John, **6**
- Dalton's Law of Partial Pressures** The total pressure exerted by a mixture of gases is the sum of the partial pressures of the individual gases, **420–426, 430, 430f, 438**
- Dative bond** A covalent bond in which both shared electrons are donated from the same atoms; a bond between a Lewis base and a Lewis acid; also known as *Coordinate covalent bond*, **990, 1010**
- Daughter nuclide** A nuclide that is produced in a nuclear decay, **865, 882**
- Davisson, C., **144**
- Davy, Humphry, **117**
- DDT, **870, 912t**
- De Broglie equation, **144–145**
- De Broglie, Louis, **144**
- Debye** The unit used to express dipole moments, **280**
- Decomposition reaction** Reaction in which a compound decomposes to form two or more products (elements, compounds, or some combination of these), **16f, 226–227, 227f, 239t, 240**
- Degenerate orbitals** Two or more orbitals that have the same energy, **155, 163, 343**
- Dehydration** The reaction in which $H-$ and $-OH$ are eliminated from adjacent carbon atoms to form water and a more unsaturated bond, **943**
- Dehydrohalogenation** An elimination reaction in which a hydrogen halide, HX ($X = Cl, Br, I$) is eliminated from a haloalkane. A $C=C$ double bond is formed, **943**
- Delocalization** The formation of a set of molecular orbitals that extend over more than two atoms; important in species that valence bond theory describes in terms of resonance (see Section 7-6), **341–342, 342f, 343**
- Delocalization of electrons** Refers to bonding electrons distributed among more than two atoms that are bonded together; occurs in species that exhibit resonance, **275, 280**
- Democritus, **5**
- Denatured enzymes, **977**
- Density** Mass per unit volume, $D=m/V$, **26–28, 35**
- metallic solids, **485**
- percent solute and, **99**
- Deposition** The direct solidification of a vapor by cooling; the reverse of sublimation, **494**

Detection of radiation, 861–862, 862f

Detergent A soap-like emulsifier that contains a sulfonate, $-\text{SO}_3^-$, or sulfate, $-\text{OSO}_3^-$, group instead of a carboxylate, $-\text{COO}^-$, group, 539, **541**, **542**, 914, 935, 970

Deviations from Raoult's Law, 520–521

Dextrorotatory Describes an optically active substance that rotates the plane of plane-polarized light to the right (clockwise); also called *dextro*, 957, 1004–1005, **1010**

Diagonal similarities Chemical similarities of elements of Period 2 to elements of Period 3 one group to the right; especially evident toward the left of the periodic table, **1040**, **1053**

Diamagnetism Weak repulsion by a magnetic field; associated with all electrons in an atom, molecule, or substance being paired, **161**–162, 161f, **163**

Diamond, 488–489, 489f

Diatomic molecules, 7

energy level diagrams, 333–334, 334f

heteronuclear, 339–340, 339f, 340f, 341f

homonuclear, 335–339, 336f, 337t

Diffusion The movement of a substance (e.g., a gas) into a space or the mixing of one substance (e.g., a gas) with another, **433**–434, 434f, **438**, 452f

Dilution The process of reducing the concentration of a solute in solution, usually simply by adding more solvent, 102–103, **106**, 520

Dimensional analysis, 22–26

Dimethyl ether, 84, 559–560

Dinitrogen oxide, 1073

Dinitrogen pentoxide, 614

Dinitrogen tetroxide, 1074

Dipeptide A compound in which two amino acid monomers have joined to form the peptide, **975**, **982**

Dipole Refers to the separation of charge between two covalently bonded atoms, **276**, **280**

Dipole-dipole interactions Interactions between polar molecules, that is, between molecules with permanent dipoles, 453–454, 454f, **494**

hydrogen bonding, 454–455, 455f

Dipole moment (μ) The product of the distance separating opposite charges of equal magnitude and the magnitude of the charge; a measure of the polarity of a bond or molecule. A measured dipole moment refers to the dipole moment of an entire molecule, **278**, **280**

Disaccharide, 972–973, 972–973f

Dispersal of energy The degree to which the total energy of a system can be distributed among its particles, **580**–581, 581f, **598**

Dispersal of matter The degree to which the particles of a sample can be distributed among its particles, **581**–582, 582–583f, **598**

Dispersed phase The solute-like species in a colloid, **535**, **542**

Dispersing medium The solvent-like phase in a colloid, **535**, **542**

Dispersion. *see* **Colloid**

Dispersion forces Very weak and very short-range attractive forces between short-lived temporary (induced) dipoles; also known as *London forces* or *van der Waals forces*, 437, 437t, **456**–458, 457f, 458t, **494**

Displacement reaction A reaction in which one element displaces another from a compound, 227–228f, **227**–232, 229t, 231f, 239t, **240**

troublesome, 230

Disproportionation reaction A redox reaction in which the oxidizing agent and the reducing agent are the same element, 223, 240

Dissociation In aqueous solution, the process in which a solid ionic compound separates into its ions, **208**, **240**, **367**

of electrolytes and colligative properties, 527–531, 528f, 529t

Dissociation constant (K_θ) The equilibrium constant that applies to the dissociation of a complex ion into a simple ion and a coordinating species (ligands), **797**

Dissolution

effect of pressure on solubility in, 515, 515f

effect of temperature on solubility in,

514–515, 514f

of gases in liquids, 512–513, 512f

of liquids in liquids, 510–511, 510t, 511f

precipitate, 795–796

rates of saturation and, 513

of solids in liquids, 508–510, 509f

spontaneity, 506–508, 507f

Distillation The separation of a liquid mixture into its components on the basis of differences in boiling points; the process in which components of a mixture are separated by boiling away the more volatile liquid, 464, 464f, **465**, **494**, **542**

fractional, 522–523, 522–523f

DNA Deoxyribonucleic acid; a nucleic acid consisting of phosphate, 2-deoxyribose, and the four bases adenine, cytosine, guanine, and thymine, 978–981, 980–981f, **982**

Δ_{oct} The energy separation between e_g and t_{2g} sets of metal d orbitals caused by six ligands bonding in an octahedral geometry, **1010**

Donor atom A ligand atom whose electrons are shared with a Lewis acid, 994, 994t, **1010**

d orbitals Beginning in the third shell, a set of five degenerate orbitals per shell, higher in energy than s and p orbitals in the same shell, 156–157, **163**

Double bond A covalent bond resulting from the sharing of four electrons (two pairs) between two atoms, 259, 259f, **280**, 317–319, 320–321f

Downs cell An electrolytic cell for the commercial electrolysis of molten sodium chloride, 806–807, 806f, **842**

Dry cell Ordinary batteries (voltaic cells) for flashlights, radios, and so on; many are Leclanché cells, 837–838, 837–838f, **842**

d -Transition elements (metals) The B group elements in the periodic table; sometimes

called simply transition elements, **176**, **201**, 255, 1036, 1048, **1053**

chromium oxides, oxanions, and

hydroxides, 1050–1051, 1051t

general properties, 1049, 1049t

oxidation states, 1049–1050, 1050t

Dynamic equilibrium A situation in which two (or more) processes occur at the same rate so that no *net* change occurs, 462, **494**, **668**, **700**

Effective collision A collision between molecules that results in reaction; one in which molecules collide with proper orientations and with sufficient energy to react, **638**, 638f, **656**

Effective molality The sum of the molalities of all solute particles in solution, **542**

Effective nuclear charge (Z_{eff}) The nuclear charge experienced by the outermost electrons of an atom; the actual nuclear charge minus the effects of shielding due to inner shell electrons, **177**, **201**

Effusion The escape of a gas through a tiny hole or a thin porous wall, **433**–434, 434f, **438**

e_g orbitals A set of $d_{x^2-y^2}$ orbitals in an octahedral complex; those d orbitals within a set with lobes directed along the x , y , and z axes, **1006**, **1010**

Einstein, Albert, 5, 138, 855

Electrical conduction, 804, 805f

Electrochemistry The study of the chemical changes produced by electric current and the production of electricity by chemical reactions, **804**, **842**

corrosion, 825–826f, 825–827

effect of concentrations, 827–836, 833–834f

electrical conduction, 805, 805f

electrodes, 805

primary voltaic cells and, 836–838, 837–838f

standard electrode potentials, 816–827,

817–819f, 821t, 823t, 825–826f

voltaic or galvanic cells, 811–816, 812–813f

Electrode potentials Potentials, E , of half-reactions as reductions *versus* the standard hydrogen electrode, **842**

Electrodes Surfaces on which oxidation and reduction half-reactions occur in electrochemical cells, **804**, **805**, **842**

Electrolysis The process that occurs in electrolytic cells, 15, 15f, **805**, **842**

of aqueous sodium chloride, 807, 807f

of aqueous sodium sulfate, 808, 808f

coulometry and Faraday's Law of, 808–811,

809t

of molten sodium chloride, 806–807, 806f

Electrolyte A substance whose aqueous solutions conduct electricity due to ions in solution. Acids, bases, and soluble salts are electrolytes; compounds that ionize (or dissociate into their constituent ions) when dissolved in water to produce aqueous solutions that conduct an electric current, 208–209, 209f, **240**, **367**, **742**. *see also* **Strong electrolyte**

colligative properties and dissociation of,

527–531, 528f, 529t

Unless otherwise noted, all content on this page is © Cengage Learning.

Electrolytic cell An electrochemical cell in which electrical energy causes a nonspontaneous (reactant-favored) redox reaction to occur, **805, 842**
commercial applications, **811**

Electrolytic conduction. *see* **Ionic conduction**

Electromagnetic radiation Energy that is propagated by means of electric and magnetic fields that oscillate in directions perpendicular to the direction of travel of the energy, **134–137, 163**

Electron A subatomic particle having a mass of 0.00054858 amu and a charge of $1-$, **117, 163**
cloud, **149f**
counting, **808–811, 809t**
density, **150f**
discovery of, **164–165, 166f**
paramagnetism and diamagnetism, **161–162, 162f**
spin, **152f**
unpaired, **161**
wave nature of, **144–145**

Electron capture Absorption of an electron from the first energy level (*K shell*) by a proton as it is converted to a neutron; also known as *K capture*; *positron emission*, **859–860, 882**

Electron configuration The specific distribution of electrons in the atomic orbitals of atoms and ions, **147, 153–158, 163, A-10**
periodic table and, **159–161, 160f, 161f**

Electron-deficient compound A compound containing at least one atom (other than H) that has fewer than eight valence shell electrons, **271, 280**

Electronegativity (EN) A measure of the relative tendency of an atom to attract electrons to itself when chemically combined with another atom, **186–187, 186f, 201, 252, 253, 295**

Electron group A group of valence shell electrons that determines the electronic geometry on a central atom. Can be a single bond, double bond, triple bond, or lone pair, **290, 291t, 322**

Electronic geometry The geometric arrangement of the bonding and lone pair (unshared pair) electron groups around the central atom of a molecule or polyatomic ion. This arrangement minimizes the repulsions among the electron groups. Each electronic geometry implies a particular hybridization on the central atom, **290, 291t, 294t, 295–297, 320, 321t, 322**

lone pairs on central atom, **315–317, 316t**
octahedral, **314–315**
tetrahedral, **297–310**
trigonal bipyramidal, **310–313**
trigonal planar, **297–299**

Electron transition The transfer of an electron from one energy level to another, **163**

Electroplating Plating a metal onto a (cathodic) surface by electrolysis, **842**

Elementary step An individual step in the mechanism by which a reaction occurs. For each elementary step, the reaction orders *do* match the reactant coefficients in that step, **640, 656**

Element A substance that cannot be decomposed into simpler substances by chemical means, **15, 35**
artificial transmutations of, **871–874, 872–873f**
atomic radii, **177–179, 178f**
combination reactions, **225–226, 225t**
decomposition reactions, **226–227, 227f**
displacement reactions, **227–228f, 227–229, 229t**
in the earth's crust, oceans, and atmosphere, **17, 17t**
electron affinity, **182–183**
electronegativity, **186–187, 186f**
ionic radii, **184–185, 184f, 185f**
ionization energy, **179–182**
mass of one mole of atoms of, **52–53, 53f, 53t**
names, **18**
oxidation states, **187–189, 188t**
periodic table of, **129–134**
symbols, **16**
trace, **1038–1039**

Elimination reaction A reaction in which the number of groups attached to carbon *decreases*. The degree of unsaturation in the molecule increases, **937–938, 937f, 943**

Emission spectrum The spectrum associated with emission of electromagnetic radiation by atoms (or other species) resulting from electron transitions from higher to lower energy states, **134, 139, 140f, 163**

Empirical formula. **61, 65, 72**

Emulsifier. *see* **Emulsifying agent**

Emulsifying agent A substance that coats the particles of a dispersed phase and prevents coagulation of colloidal particles; an emulsifier; also known as an *emulsifier*, **539–541, 542**

Emulsion A colloidal dispersion of a liquid in a liquid, **542**

Enantiomers Stereoisomers that differ only by being nonsuperimposable mirror images of each other; like left and right hands; also known as *optical isomers*, **956, 982, 1003–1005, 1004–1005f, 1010**

Endothermic process Describes processes that absorb heat energy, **4, 31, 35, 553, 598**

End point The point at which an indicator changes color and a titration is stopped, **380, 381f, 393, 765, 772**

Energy The capacity to do work or transfer heat. *see also* **Ionization energy**
activation, **639, 645–647**
bond dissociation, **259–260, 260t, 280**
change, free, **591–594**
changes in internal, **571–576, 572–574f, 576–577f**
chemical and physical changes and release of, **12, 13f**
defined, **4, 35**

dispersal of, **580–581, 581f**
kinetic, **4, 428–429, 429f**
law of conservation of, **4–5**
law of conservation of matter and, **5**
level diagrams, molecular orbital, **333–334, 334f**
of light, **137, 139**
matter and, **4–5**
nuclear, **878–879**
potential, **4**
solar, **851**

Enthalpy change, ΔH The quantity of heat transferred into or out of a system as it undergoes a chemical or physical change at constant temperature and pressure, **556, 598**

Enthalpy of fusion. *see* **Heat of fusion**

Enthalpy of solidification. *see* **Heat of solidification**

Entropy (S) A thermodynamic state function that measures the dispersal of energy and the dispersal of matter (disorder) of a system, **583–589, 584f, 586–587f, 588t, 598**

Enzyme A protein that acts as a catalyst in a biological system, **653, 653f, 656, 975, 982**
denatured, **977**

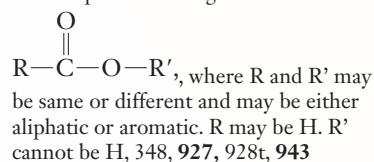
Equilibrium A state of dynamic balance in which the rates of forward and reverse processes (reactions) are equal; the state of a system when neither the forward nor the reverse process is thermodynamically favored, **32, 33f, 598. see also Chemical equilibrium**
heterogeneous, **694–695**
simultaneous, **792–794**

Equilibrium constant (K) A dimensionless quantity that indicates the extent to which a reversible reaction occurs. *K* varies with temperature, **670–673**
evaluation at different temperatures, **699**
partial pressures and, **691–692**
relationship between ΔG_{rxn}^0 and, **695–698, 697f**
relationship between K_p , **692–694**
uses of, **676–679**
variation with the form of the balanced equation, **673–674**

Equilibrium constant (K) A dimensionless quantity that indicates the extent to which a reversible reaction occurs. *K* varies with temperature, **700**

Equivalence point The point at which chemically equivalent amounts of reactants have reacted, **380, 393, 765, 772**

Ester A compound of the general formula



Ethane, **890, 891f**

Ethanol, **463, 468, 563, 565, 575–576**

Ethers, **918, 918f**

Ethyl alcohol, 7f, 465, 913, 918, 1037
density, 28f

Ethylene, 267, 565

Ethylene glycol, 45, 465, 526, 916, 918, 940

Ethyl iodide, 646

Eutrophication The undesirable overgrowth of vegetation caused by high concentration of plant nutrients in bodies of water, **541, 543**

Evaporation The process by which molecules on the surface of a liquid break away and go into the gas phase, 461–462, 462f, 465, **494**

Excited state Any energy state other than the ground state of an atom, ion, or molecule, **163**

Exothermic process Describes processes that release heat energy, **4, 31, 35, 553, 579, 598, 611f**

Expanded valence shell Describes a Group A (representative) atom that contains more than eight valence shell electrons, 272, **280**

Extensive property A property that depends on the amount of material in a sample, **11, 35**

Factor-label method, 22–26

Fahrenheit, Gabriel, 29

Fahrenheit scale, 29–31, 30f

Faraday An amount of charge equal to 96,485 coulombs; corresponds to the charge on one mole of electrons, 6.022×10^{23} electrons, 809, **842**

Faraday's Law of Electrolysis The amount of substance that undergoes oxidation or reduction at each electrode during electrolysis is directly proportional to the amount of electricity that passes through the cell, 808–811, 809t, **842**

Faraday, Michael, 117, 808f

Fast neutron A neutron ejected at high kinetic energy in a nuclear reaction, **874, 882**

Fat A solid triester of glycerol and (mostly) saturated fatty acids, **927–928, 943**

Fatty acid A long-chain aliphatic acid; many can be obtained from animal fats, **927, 943**

Ferromagnetism The property that allows a substance to become permanently magnetized when placed in a magnetic field; exhibited by iron, cobalt, and nickel and some of their alloys, **163**

First Law of Thermodynamics The total amount of energy in the universe is constant (also known as the *Law of Conservation of Energy*); energy is neither created nor destroyed in ordinary chemical reactions and physical changes, **553–554, 554f, 572, 598**

First-order reactions, 627–628, 630f, 632

Flotation A method by which hydrophobic (water-repelling) particles of an ore are separated from hydrophilic (water-attracting) particles in a metallurgical pretreatment process, **1019, 1030**

Fluids, 402

Fluorescence Absorption of high-energy radiation by a substance and the subsequent emission of visible light, **861, 882**

Fluorine, 7f, 1061
molecule, 338

Flux A substance added to react with or dissolve the charge, or a product of its reduction, in metallurgy; usually added to lower a melting point, **1030**

Foam A colloidal dispersion of a gas in a liquid, **543**

f orbitals Beginning in the fourth shell, a set of seven degenerate orbitals per shell, higher in energy than *s*, *p*, and *d* orbitals in the same shell, 152f, **163**

Formal charge The hypothetical charge on an atom in a covalently bonded molecule or ion; bonding electrons are counted as though they were shared equally between the two bonded atoms, **267–269, 280**

Formaldehyde, 918–920

Formula Combination of element symbols that indicates the chemical composition of a substance, **60–61, 72. see also simplest formula**

Formula unit The smallest repeating unit of a substance—for non-ionic substances, the molecule, **72**

Formula unit equation An equation for a chemical reaction in which all formulas are written as complete formulas, **240, 367**

Formula weight The mass, in atomic mass units, of one formula unit of a substance. Numerically equal to the mass, in grams, of one mole of the substance (*see* Molar mass). This number is obtained by adding the atomic weights of the atoms specified in the formula, **56–59, 72**

Fossil fuels, 199–200, 199f, 200f, 200t, 879, 900

Fractional distillation The process in which a fractionating column is used in a distillation apparatus to separate components of a liquid mixture that have different boiling points, **522–523, 522–523f, 543**

Fractional precipitation Removal of some ions from solution by precipitation while leaving other ions, with similar properties, in solution, **790–792, 797**

Frasch process A method by which elemental sulfur is mined or extracted. Sulfur is melted with superheated water (at 170°C under high pressure) and forced to the surface of the earth as a slurry, 1057f, **1066, 1080**

Free energy change, 591–594

Free halogens, 1062–1063

Free metals, reduction to, 1021–1022t

Freezing point. see Melting point

Freezing point depression The decrease in the freezing point of a solvent caused by the presence of a solute, **525–526, 543**
determination of molecular weight by, 526–527

Freezing point depression constant, K_f A constant that corresponds to the change in freezing point produced by a one-

molal ideal solution of a nonvolatile nonelectrolyte, **543**

Frequency (ν) The number of crests of a wave that pass a given point per unit time, **134, 163**

Fructose, 66f, 127, 972

f-Transition elements (metals) Elements 58 through 71 and 90 through 103; also called inner transition elements (metals), **176, 201**

Fuel cell A voltaic cell in which the reactants (usually gases) are supplied continuously and products are removed continuously, **840–841, 841f, 842**

Functional group A group of atoms that represents a potential reaction site in an organic compound, **890, 911, 930–931, 931f, 943**

alcohols and phenols, 913–918, 913f, 917f, 917t

aldehydes and ketones, 918–920, 919f, 919t, 921t

amines, 921–922, 922f

carboxylic acids, 922–930, 923f, 923t, 926f, 926t, 927f, 928t, 929f

ethers, 918, 918f

organic halides, 911–913, 912t

Fundamental particles Subatomic particles of which all matter is composed; protons, electrons, and neutrons are fundamental particles, **6, 6, 6f, 163–164**

mass spectrometry and isotopic abundance, **124–125, 125f, 126f**

Fundamental step. see Elementary step

Gallium, 1045t, 1046

Galvanic cell, 811–812, 812f. see Voltaic cell

Gamma ray (γ) High-energy electromagnetic radiation, **857, 858t, 882**

irradiation, 870, 871f

Gangue Sand, rock, and other impurities surrounding the mineral of interest in an ore, **1018, 1030**

Gases, 10, 10f, 401–438

Avogadro's Law and Standard Molar Volume, 414–415, 414t

Boyle's law, 405–410, 408f

Charles' law, 410–412

collected over water, 425–426

Combined Gas Law equation, 412–413

composition of the atmosphere and common properties of, 403, 403t

Dalton's Law of Partial Pressures, 420–426
deviations from ideal gas behavior, 435–436f, 435–437, 437t

diffusion and effusion of, 433–434, 434f

dissolution in liquids, 512–513, 512f

kinetic-molecular description of, 450–451, 451f

kinetic-molecular theory, 428–433, 429–431f

mass-volume relationships in reactions

involving gases, 426–428, 426f, 427f

molecular weights and molecular formulas, 419–420

phase diagrams, 472–475, 473–475f

pressure, 403–405, 403f–405f

standard temperature and pressure, 412

Unless otherwise noted, all content on this page is © Cengage Learning.

- Gas-formation reaction** A reaction in which an insoluble or slightly soluble gas is formed as a product, **237–238**, **239t**, **240**
- Gas ionization counters, **862**, **862f**
- Gay-Lussac, Joseph, **349**, **410**
- Gay-Lussac's Law of Combining Volumes**
At constant temperature and pressure, the volumes of gases that react or are formed can be expressed as ratios of small whole numbers, **427**, **438**
- Geiger-Müller counter** A type of gas ionization counter used to detect radiation, **862**, **862f**, **882**
- Gel** A colloidal dispersion of a solid in a liquid; a semirigid sol, **539**, **539f**, **543**
- Geometric isomerism** Occurs when atoms or groups of atoms can be arranged in different ways on two sides of a rigid structure; also known as *cis-trans* isomerism. In geometric isomers of coordination compounds, the same ligands are arranged in different orders within the coordination sphere, **1010**
- Geometric isomers** Compounds with different arrangements of groups on the opposite sides of a bond with restricted rotation, such as a double bond; for example, *cis-trans* isomers of certain alkenes, **899**, **943**, **955–956**, **956f**, **982**
- coordination compounds, **1000–1003**, **1002f**
- Germanium, **131t**
- Germer, L. H., **144**
- Gibbs free energy (G)** The thermodynamic state function of a system that indicates the amount of energy available for the system to do useful work at constant *T* and *P*. It is defined as $G = H - TS$; also known as *free energy*, **598**
- relationship between equilibrium constant and, **695–698**, **697f**
- relationship between standard cell potential and, **835–836**
- Glass electrode** An electrode consisting of an AgCl-coated silver wire in contact with an HCl solution of known standard concentration (usually **1.00 M**) in a thin-walled glass bulb; when immersed in a solution, this electrode develops a potential that is sensitive to the relative $[H^+]$ concentrations (and hence to pH differences) of the internal standard solution and the outside solution, **833**, **833f**, **842**
- Glucose, **64f**, **66**, **66f**
- Glutathione, **975**
- Glyceride** A triester of glycerol, **928**, **943**
- Glycine, **959**
- Glycosidic bond** A bond linking monomers in a polysaccharide, **972–973**, **972–973f**, **982**
- Gold, **811**, **1029**
- Goldstein, Eugen, **119**
- Graham, Thomas, **403**
- Graphite, **489**, **489f**, **561**, **564–565**
- Greenhouse effect, **406–407**
- Ground state** The lowest energy state or most stable state of an atom, molecule, or ion, **153**, **163**
- Group (family)** The elements in a vertical column of the periodic table, **132–133**, **163**, **240**
- Group 1A elements. *see* **Alkali metals**
- Group 2A elements. *see* **Alkaline earth metals**
- Group 3A elements. *see* **Post-transition metal**
- Group 5A elements
nitrogen, **1071–1077**, **1071t**, **1072f**, **1073–1074f**, **1077f**
phosphorus, **1077–1078**, **1077–1078f**
- Group 6A elements
hydrides of, **1067**
occurrence, properties, and uses, **1065–1066**, **1066t**, **1067f**
oxides, **1068–1069**, **1068f**
reactions, **1067**
- Group 7A elements. *see* **Halogens**
- Group 8A elements. *see* **Noble (rare) gases**
- Haber process** An industrial process for the catalyzed production of ammonia from N_2 and H_2 at high temperature and pressure (see Section 17-7), **686–688**, **687f**, **687t**, **1080**
- Half-cell** The compartment in a voltaic cell in which the oxidation or reduction half-reaction occurs, **812–813**, **813f**, **842**
- Half-life of a radionuclide** The time required for half of a given sample to undergo radioactive decay, **863–864**, **864–865f**, **866t**, **882**
- Half-life of a reactant ($t_{1/2}$)** The time required for half of that reactant to be converted into product(s), **627**, **629**, **632t**, **656**
- Half-reaction** Either the oxidation part or the reduction part of a redox reaction, **393**, **823–825**, **823t**
- Half-wavelengths, **146**
- Halides** Binary compounds of the halogens with less electronegative elements, **911–913**, **912t**, **1080**
- hydrogen, **365**, **1063–1064**, **1064f**
- Hall-Héroult process** A process in which a molten mixture of Al_2O_3 , NaF, and AlF_3 is electrolyzed to obtain pure aluminum, **1030**
- Halogenation reaction** A substitution reaction in which a hydrogen atom is replaced by a halogen atom, **932–935**, **943**
- Halogens** Elements of Group 7A in the periodic table, **131f**, **133**, **163**, **240**, **1059–1060**, **1060t**, **1080**
- hydrogen halides and hydrohalic acids, **365**, **1063–1064**, **1064f**
occurrence, production, and uses, **1061–1062**
oxidation states, **189**
oxoacids of, **1064–1065**, **1065t**
properties, **1060–1061**, **1060t**
reactions of free, **1062–1063**
reactions with alkali metals, **252–254**
- Hard water** Water containing Fe^{3+} , Ca^{2+} , or Mg^{2+} ions, which form precipitates with soaps, **541**, **543**
- Heat** A form of energy that flows between two samples of matter because of their difference in temperature, **29–31**, **35**
- enthalpy changes, **556**
of formation, **562–563**
heat transfer and measurement of, **31–34**
Hess's Law, **564–568**
specific, **31–34**
transfer involving liquids, **465–469**, **465t**, **467f**, **468t**
transfer involving solids, **469–472**, **470f**, **470t**
transfer measurement, **556–558**, **557f**
- Heat capacity** The amount of heat required to raise the temperature of a body one degree Celsius, **32**, **35**
- Heat of combustion** The amount of energy liberated per mole of substance burned, **967**, **982**
- Heat of condensation** The amount of heat that must be removed from a specific amount of a vapor as its condensation point to condense the vapor with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the molar heat of condensation, **495**
- Heat of formation.** *see* **Standard molar enthalpy of formation**
- Heat of fusion** The amount of heat required to melt a specific amount of a solid at its melting point with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the molar heat of fusion, **470t**, **471–472**, **495**
- Heat of hydration.** *see* **Hydration energy (molar) of an ion**
- Heat of solidification** The amount of heat that must be removed from a specific amount of a liquid at its freezing point to freeze it with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the molar heat of solidification, **471**, **495**
- Heat of solution (molar)** The amount of heat absorbed in the formation of a solution that contains one mole of solute; the value is positive if heat is absorbed (endothermic) and negative if heat is released (exothermic), **507**, **543**
- Heat of vaporization** The amount of heat required to vaporize a specific amount of a liquid at its boiling point with no change in temperature; usually expressed in J/g or kJ/mol; in the latter case it is called the molar heat of vaporization, **466–467**, **495**
- Heavy water** Water containing deuterium, a heavy isotope of hydrogen, 2H , **877**, **882**
- Heisenberg, Werner**, **146**
- Heisenberg Uncertainty Principle** It is impossible to determine accurately both the momentum and position of an electron simultaneously, **146**, **163**
- Helium, **336**, **336f**, **416–417**
- Hemoglobin, **991**
- Henderson-Hasselbach equation** An equation that enables us to calculate the pH or pOH of a buffer solution directly, **753–754**, **772**
- For acid/salt buffer $pH = pK_a + \log \frac{[\text{conj. base}]}{[\text{acid}]}$
- For base/salt buffer $pOH = pK_b + \log \frac{[\text{conj. acid}]}{[\text{base}]}$

- Henry's Law** The concentration or solubility of a gas in a liquid at any given temperature is directly proportional to the partial pressure of the gas over the solution, **515**, **515f**, **543**
- Heptane, **519**, **520**
- Hertz, Heinrich, **134**
- Hess, G. H., **564**
- Hess's Law of Heat Summation** The enthalpy change for a reaction is the same whether it occurs in one step or a series of steps, **564–568**, **569**, **583**, **598**
- Heteroatom** An atom other than C or H in an organic molecule; the most common heteroatoms are O, N, S, P, and the halogens, **943**
- Heterocyclic amine** An amine in which nitrogen is part of a ring, **943**
- Heterogeneous catalyst** A catalyst that exists in a different phase (solid, liquid, or gas) from the reactants; the vast majority of heterogeneous catalysts are solids, **649–653**, **650–652f**, **656**
- Heterogeneous equilibria** Equilibria involving species in more than one phase, **694–695**, **700**
- Heterogenous mixture** A mixture that does not have uniform composition and properties throughout, **13**, **13f**, **14f**, **35**
- Heteronuclear** Consisting of different elements, **276**, **280**, **343**
- diatomic molecules, **339–340**, **339f**, **340f**, **341f**
- High spin complex** A complex in which the crystal field splitting energy is smaller than the pairing energy so that all *d* orbitals are singly occupied before pairing occurs; there are the same number of unpaired *d* electrons on the metal atom as when the metal is uncomplexed. In an octahedral high spin complex, all *t_{2g}* and *e_g* orbitals are singly occupied before any pairing occurs, **1007**, **1010**
- Homogeneous catalyst** A catalyst that exists in the same phase (liquid or gas) as the reactants, **648–649**, **656**
- Homogeneous mixture** A mixture that has uniform composition and properties throughout, **13**, **13f**, **35**, **506**
- Homologous series** A series of compound in which each member differs from the next by a specific number and kind of atoms, **892**, **943**
- Homonuclear** Consisting of only one element, **280**, **333**, **343**
- diatomic molecules, **335–339**, **336f**, **337t**
- Hund's Rule** Each orbital of a given subshell is occupied by a single electron before pairing begins. See Aufbau Principle, **155**, **158**, **163**, **296**, **333**
- Hybridization** The mixing of a set of atomic orbitals on an atom to form a new set of hybrid orbitals with the same total electron capacity and with properties and energies intermediate between those of the original unhybridized orbitals, **294**, **294t**, **297**, **322**
- of carbon in covalent bond formation, **889**, **889t**
- Hybrid orbitals** Orbitals formed on an atom by the process of hybridization, **294**, **296**, **314**, **322**
- Hydrate** A crystalline sample that contains water, H₂O, and another compound in a fixed mole ratio. Examples include CuSO₄·5H₂O and (COOH)₂·2H₂O, **69**, **72**
- isomers, **999–1000**
- Hydrate isomers** Isomers of crystalline complexes that differ in terms of the presence of water inside or outside the coordination sphere, **1010**
- Hydration** The interaction (surrounding) of solute particles with water molecules, **508–510**, **543**
- Hydration energy (molar) of an ion** The energy change accompanying the hydration of a mole of gaseous ions, **508**, **543**
- Hydration reaction** A reaction in which the elements of water, H and OH, add across a double or triple bond, **943**
- Hydride** A binary compound of hydrogen, **367**
- boiling point, **455**, **455f**
- of group 6A elements, **1067**
- periodicity, **190–193**
- Hydrocarbon** A compound that contains only carbon and hydrogen, **890**, **910–911f**, **943**.
- see also **Aliphatic hydrogens**; **Aromatic hydrocarbons**; **Saturated hydrocarbons**; **Unsaturated hydrocarbons**
- Hydrochloric acid, **348**, **361f**, **376**
- Hydrofluoric acid, **210**, **724**, **1064**, **1079**
- Hydrogen, **7f**
- balancing redox reactions and, **388–390**
- chemical reactions and periodicity, **190–193**
- compounds of nitrogen, **1072–1073**, **1073f**
- covalent bonds, **258**, **258f**
- isotopes, **123f**
- molecule, **336**, **336f**
- oxidation state, **188**
- Hydrogenation** The reaction in which hydrogen adds across a double or triple bond, **936**, **943**
- Hydrogen bond** A fairly strong dipole-dipole interaction (but still considerably weaker than covalent or ionic bonds) between molecules containing hydrogen directly bonded to a small, highly electronegative atom, such as N, O, or F, **495**
- dipole-dipole interaction, **454–455**, **455f**
- Hydrogen chloride, **85–86**
- Hydrogen fluoride, **340**, **340f**, **341f**
- Hydrogen halides, **365**, **1063–1064**, **1064f**
- dissolution, **512**
- Hydrogen-oxygen fuel cell** A fuel cell in which hydrogen is the fuel (reducing agent) and oxygen is the oxidizing agent, **840–841**, **841f**, **842**
- Hydrohalic acids, **355–356**, **365–366**, **512**, **1063–1064**, **1064f**
- Hydrolysis** The reaction of a substance with water, **732**, **733–736**, **742**, **962**
- effect on solubility, **787**
- of esters, **969–970**, **970f**
- Hydrolysis constant** An equilibrium constant for a hydrolysis reaction, **742**
- Hydronium ion** H₃O⁺, the usual representation of the hydrated hydrogen ion, **350**, **367**
- Hydrophilic colloids** Colloidal particles that repel water molecules, **539**, **543**
- Hydroxides, **1050–1051**, **1051t**
- metal, **993**, **994t**
- Hypervalent. see **Expanded valence shell**
- Ideal gas** A hypothetical gas that obeys exactly all postulates of the kinetic-molecular theory, **415**, **438**
- deviations, **435–436f**, **435–437**, **437t**
- Ideal gas equation** The product of the pressure and volume of an ideal gas is directly proportional to the number of moles of the gas and the absolute temperature, **415–418**, **431–433**, **438**
- Ideal solution** A solution that obeys Raoult's Law exactly, **519**, **543**
- Indicator** (for acid-base reaction) An organic compound that exhibits different colors in solutions of different acidities; used to indicate the point at which reaction between an acid and a base is complete, **380**, **384f**, **393**, **716**, **763–765**, **766t**, **772**
- Indium, **1045t**, **1047**
- Inert electrode** An electrode that does not take part in the electrochemical reaction, **842**
- Inert s-pair effect** The tendency of the two outermost *s* electrons to remain nonionized or unshared in compounds; characteristic of the post-transition metals, **1053**
- Inner transition elements. see **f-Transition elements (metals)**
- Inorganic chemistry
- defined, **3**
- Inorganic compounds, **44**
- naming, **217–218**, **219t**
- Insoluble bases, **212**
- Insulator** A poor conductor of electricity and heat, **491**, **491f**, **495**
- Integrated rate equation** An equation that relates the concentration of a reactant remaining to the time elapsed; has different mathematical forms for different orders of reaction, **627–637**, **630f**, **632t**, **633–637**, **656**
- Intensive property** A property that is independent of the amount of material in a sample, **11**, **35**
- Intermolecular forces** Forces between individual particles (atoms, molecules, ions) of a substance, **452**, **495**
- boiling points *versus*, **469**
- dissolution and, **507–508**
- phase changes and, **451–458**, **452f**, **453t**, **454–456f**, **457t**
- physical properties of liquids and, **468t**
- Internal energy (E)** All forms of energy associated with a specific amount of a substance, **571–576**, **572–574f**, **576–577f**, **598**

- Intramolecular forces** Forces between atoms (or ions) within molecules (or formula units), **452, 495**
- Iodine, **7f, 10f, 1062**
- Iodine-123, **868, 870**
- Iodine chloride, **616–617**
- Ion** An atom or group of atoms that carries an electric charge. A positive ion is a cation; a negative ion is an anion, **48–49, 48f, 49t, 73, 280**
- Ionic bonding** The attraction of oppositely charged ions (cations and anions) in large numbers to form a solid. Ions result from the transfer of one or more electrons from one atom or group of atoms to another, **250, 251, 280, 486–488, 486–488f**
- Ionic compound** A compound that is composed of cations and anions. An example is sodium chloride, NaCl, **48–49, 48f, 49t, 73, 280**
- binary, **217–218, 219t, 255–256, 256t**
- formation, **251–257, 252f, 254f, 256t**
- names and formulas of, **49–51**
- solubility guidelines for common, **213, 214t**
- Ionic conduction** Conduction of electric current by ions through a pure liquid or a solution; also known as *Electrolytic conduction*, **805, 805f, 842**
- Ionic hydride** An ionic compound that contains the hydride ion, H₂, **191, 201**
- Ionic radius** The radius of an ion, **184–185, 184f, 185f, 201, 487–488**
- Ion-ion interactions, **453, 453t**
- Ionization** In aqueous solution, the process in which a molecular compound separates to form ions, **208–209, 240, 367**
- constants for weak monoprotic acids and bases, **717–729**
- isomers, **999**
- Ionization constant** An equilibrium constant for the ionization of a weak electrolyte, **717–729, 742**
- Ionization energy** The amount of energy required to remove the most loosely held electron of an isolated gaseous atom or ion, **179–182, 180f, 201**
- Ionization isomers** Isomers that result from the interchange of ions inside and outside the coordination sphere, **1010**
- Ion product for water** An equilibrium constant for the ionization of water, $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ at 25°C, **711, 742**
- Iron, **14f, 1026–1027, 1027t, 1028f**
- deficiency, **1038**
- Isoelectronic** Having the same number of electrons, **184, 201**
- Isolated yield.** *see actual yield*
- Isomers** Different compounds that have the same molecular formula, **892, 943, 1010**
- alkanes, **893–895, 894f, 894t**
- constitutional, **954–955, 999–1000**
- in coordination compounds, **998–1005, 1002f, 1004–1005f**
- geometric, **955–956, 956f, 1000–1003, 1002f**
- optical, **956–959, 957–959f, 1003–1005, 1004–1005f**
- stereo-, **955–959, 956–959f, 1000–1005, 1002f, 1004–1005f**
- Isomorphous** Refers to crystals having the same atomic arrangement, **480, 495**
- Isotopes** Two or more forms of atoms of the same element with different masses; that is, atoms containing the same number of protons but different numbers of neutrons, **123–124, 163**
- stable, **127**
- Janet, Charles, **175, 175f**
- Joule** A unit of energy in the SI system. One joule is $1 \text{ kg} \cdot \text{m}^2/\text{s}^2$, which is also 0.2390 cal., **31, 35, 416**
- K.** *see Equilibrium constant (K)*
- K_c** Equilibrium constant with amounts of reactants and products expressed as molar concentrations, **700**
- Kelvin, Lord, **410**
- Kelvin scale, **30–31, 30f, 410–411, 411f**
- Ketone** A compound in which a carbonyl group is bound to two alkyl or two aryl groups, or to one alkyl and one aryl group, **918–920, 919f, 919t, 921t, 943, 965–966**
- Ketose** A monosaccharide that contains a ketone group, **971, 982**
- Kilogram, **20**
- Kinetic energy** The energy of motion. The kinetic energy of an object is equal to one half its mass times the square of its velocity, **4, 35, 553, 598. see also Chemical kinetics**
- Kinetic-molecular theory** A theory that attempts to explain macroscopic observations of gases in microscopic or molecular terms, **428–433, 429–431f, 435–436, 436f, 438**
- K_p** Equilibrium constant with amounts of reactants and products expressed as partial pressures, **692–694, 700**
- Lanthanides** Elements 58 through 71 (after lanthanum); also known as *rare earth elements*, **201**
- Lavoisier, Antoine, **18**
- Law of Conservation of Energy** Energy cannot be created or destroyed in a chemical reaction or in a physical change; it may be changed from one form to another; see First Law of Thermodynamics, **4–5, 35, 554, 598**
- Law of Conservation of Matter** No detectable change occurs in the total quantity of matter during a chemical reaction or during a physical change; it may be destroyed during a physical change, **4, 35, 83**
- Law of Conservation of Matter and Energy** The combined amount of matter and energy in the universe is fixed, **5, 35**
- Law of Constant Composition**, **45. see Law of Definite Proportions**
- Law of Definite Proportions** Different samples of any pure compound contain the same elements in the same proportions by mass; also known as the *Law of Constant Composition*, **16, 35, 45, 73**
- Law of Multiple Proportions** When two elements, A and B, form more than one compound, the ratio of the masses of element B that combine with a given mass of element A in each of the compounds can be expressed by small whole numbers, **67, 73**
- Lead, **567–568**
- Lead storage battery** A secondary voltaic cell that is used in most automobiles, **838–840, 839f, 842**
- LeChatelier's Principle** A system at equilibrium, or striving to attain equilibrium, responds in such a way as to counteract any stress placed upon it, **462, 495, 514, 679–681, 700**
- Leclanché cell** A common type of dry cell (battery), **837, 842**
- Length, **20–21, 21f**
- Leveling effect** The effect by which all acids stronger than the acid that is characteristic of the solvent react with the solvent to produce that acid; a similar statement applies to bases. The strongest acid (base) that can exist in a given solvent is the acid (base) characteristic of that solvent, **367**
- Levorotatory** Refers to an optically active substance that rotates the plane of plane-polarized light to the left (counterclockwise); also called *levo*, **957, 1004–1005, 1010**
- Lewis, G. N., **363**
- Lewis acid** A substance that accepts a share in a pair of electrons from another species, **270, 280, 363–365, 363–365f, 367. see also Coordination compound or complex**
- Lewis base** A substance that makes available a share in an electron pair, **270, 280, 363–365, 363–365f, 367. see also Coordination compound or complex**
- Lewis formula** The representation of a molecule, ion, or formula unit by showing atomic symbols and only outer-shell electrons; does not represent the shape of the molecule or ion. Each bonding electron pair can be represented by a pair of dots (the Lewis dot formula) or by a dash (the Lewis dash formula), **250–251, 251t, 280, 289, 322**
- electronic geometry, **295–315**
- limitations of the octet rule, **269–274**
- for molecules and polyatomic ions, **260–261**
- octet rule for writing, **261–267**
- resonance and, **274–275**
- Ligand** A Lewis base in a coordination compound, **1010**
- Light
- energy of, **137, 139**
- visible, **135–137, 136f**
- Light water reactors, **876–878, 876f**
- Limiting reactant (or reagent)** A substance that stoichiometrically limits the amount of product(s) that can be formed in a reaction, **91–94, 106**

- Linear** A term used to describe the electronic geometry around a central atom that has two electron groups. also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to two atoms on opposite sides (180°) of the central atom (AB_2 or AB_2U_3), 295–297, **322**
- Linear accelerator** A device used for accelerating charged particles along a straight-line path, **872–873**, **872–873f**, **882**
- Line spectrum** An atomic emission or absorption spectrum, **163**
- Linkage isomers** Isomers in which a particular ligand bonds to a metal ion through different donor atoms, **1000**, **1010**
- Liquid aerosol** A colloidal dispersion of a liquid in a gas, **543**
- Liquids**, **9**, **10f**
 dissolution of gases in, **512–513**, **512f**
 dissolution of liquids in, **510–511**, **510t**, **511f**
 dissolution of solids in, **508–510**, **509f**
 evaporation, **461–462**, **462f**
 heat transfer involving, **465–469**, **465t**, **467f**, **468t**
 intermolecular attractions and phase changes, **451–458**, **452f**, **453t**, **454–456f**, **457t**
 kinetic-molecular description of, **450–451**, **451f**
 phase diagrams, **472–475**, **473–475f**
 surface tension, **460**, **460f**
 vapor pressure and, **462–464**, **463f**, **464t**
 viscosity, **459**, **459f**
- Lithium**, **130f**, **254**, **1040**, **1041**, **1041f**
 reaction with water, **173f**
- Litmus**, **764**
- London forces.** *see* **Dispersion forces**
- Lone pair** A pair of electrons residing on one atom and not shared by other atoms; also known as *unshared pair*, **261–262**, **280**, **315–317**, **316t**
- Low spin complex** A complex in which the crystal field splitting energy is greater than the pairing energy so that there are the same number of fewer unpaired d electrons on the metal atom than when the metal is uncomplexed. In an octahedral low spin complex, pairing occurs to fill the t_{2g} orbitals before any electrons occupy the e_g orbitals, **1007–1008**, **1008t**, **1010**
- Lung cancer**, **869**
- Macroscale**, **5**
- Magnesium**, **4f**, **1023–1024**, **1024f**, **1044**
- Magnesium hydroxide**, **792–793**
- Magnesium nitrate**, **792–793**
- Magnetic quantum number (m_λ)** Quantum mechanical solution to a wave equation that designates the particular orbital within a given subshell (s , p , d , f) in which an electron resides. The p_x , p_y , p_z orbitals have different magnetic quantum numbers, **148**, **163**
- Manganese**, **1039**
- Manometer** A two-armed barometer, **404**, **438**
- Margarine**, **930**
- Mass** A measure of the amount of matter in an object. Mass is usually measured in grams or kilograms, **4**, **20**, **20f**, **35**. *see also* **percent by mass**
 of atoms, **55**
 calculations based on chemical equations, **89–91**
 density and, **27**
 of molecules, **58**
 percent composition and, **60**
 of solute, **99**, **100–101**
 of solution, **98**
 –volume relationships in reactions involving gases, **426–428**, **426f**, **427f**
- Mass action expression** For a reversible reaction, $aA + bB \rightleftharpoons cC + dD$ the product of the molar concentrations of the products (species on the right), each raised to the power that corresponds to its coefficient in the balanced chemical equation, divided by the product of the concentrations of the reactants (species on the left), each raised to the power that corresponds to its coefficient in the balanced chemical equation. At equilibrium the mass action expression is equal to K ; at other conditions, it is Q , **700**
- Mass deficiency (Δm)** The amount of matter that would be converted into energy if an atom were formed from constituent particles, **854–855**, **882**
- Mass number** The integral sum of the numbers of protons and neutrons in an atom, **123–124**, **163**
- Mass spectrometer** An instrument that measures the charge-to-mass ratios of charged particles, **124–125**, **125f**, **126f**, **163**
- Matter** Anything that has mass and occupies space, **4**, **35**, **402**
 chemical and physical properties, **10–11**, **12f**, **12t**
 chemistry as molecular view of, **5–9**
 dispersal of, **581–582**, **582–583f**
 energy and, **4–5**
 fundamental particles, **6**, **6f**
 law of conservation of, **4**
 law of conservation of energy and, **5**
 mixtures, substances, compounds, and elements, **13–17**
 states of, **9–10**, **10f**
- Maxwell-Boltzmann distributions**, **644**
- McMillan, E. M.**, **874**
- Measurements**
 in chemistry, **19**, **19t**
 density and specific gravity, **26–29**
 heat and temperature, **29–31**
 heat transfer, **31–34**
 length, **20–21**, **21f**
 mass and weight, **20**, **20f**, **21f**, **21t**
 percentage, **26**
 SI units, **19**, **19t**, **21t**, **23–24**
 unit factor method, **22–26**
 units of, **20–21**, **20f**, **20t**, **21f**, **21t**
 volume, **21**, **21f**, **21t**
- Melting point** The temperature at which liquid and solid coexist in equilibrium; also the freezing point, **469**, **495**, **590–591**
- Mendeleev, Dmitri**, **129–132**, **175**, **182f**, **183f**
- Meniscus** The upper surface of a liquid in a cylindrical container, **460**, **461f**, **495**
- Mercury**, **17f**, **403–404**, **1052**
- Metal** An element below and to the left of the stepwise division (metalloids) of the periodic table; about 80% of the known elements are metals, **133t**, **163**, **240**. *see also* ***d*-Transition elements (metals)**
 in aircraft construction, **1035f**
 alkali, **132**, **162**, **240**, **252–254**, **1037–1042**, **1037t**, **1040t**, **1041f**
 alkaline earth, **132**, **162**, **240**, **255**, **1042–1043**, **1042t**, **1043f**, **1043t**
 aluminum, **85–86**, **134**, **560–561**, **1024–1026**, **1025f**
 ammine complexes, **993**, **994t**
 band theory of, **489–493**, **490–491f**
 copper, **8f**, **69–70**, **558**, **811**, **822**, **1028–1029**, **1030f**
d-transition, **176**, **201**, **255**
 gold, **811**, **1029**
 hydroxides, **993**, **994t**
 iron, **1026–1027**, **1027t**, **1028f**
 magnesium, **4f**, **1023–1024**, **1024f**, **1044**
 metallurgy, **1018**, **1019t**
 occurrence of, **1018**
 reduction to free, **1021–1022t**
 refining, **1022**, **1023f**
- Metallic bonding** Bonding within metals due to the electrical attraction of positively charged metal ions for mobile electrons that belong to the crystal as a whole, **481–482f**, **481–486**, **481t**, **486f**, **489–493**, **490–491f**, **495**
- Metallic conduction** Conduction of electric current through a metal or along a metallic surface, **805**, **805f**, **842**
- Metalloids** Elements with properties intermediate between metals and nonmetals: B, Si, Ge, As, Sb, Te, Po, and At, **133**, **133f**, **134**, **163**, **240**
- Metallurgy** The overall processes by which metals are extracted from ores, **1018**, **1019t**, **1030**
- Metathesis reaction** A reaction in which the positive and negative ions in two compounds “change partners,” with no change in oxidation numbers, to form two new compounds; also referred to as a double displacement reaction, **232–237**, **233t**, **236f**, **239t**, **240**
- Meter**, **20–21**
- Methane**, **7f**, **12t**, **890**, **891f**
 combustion, **81f**, **82–83**, **83f**
- Methanol**, **92**, **463**
 dissolution, **510–511**
- Method of initial rates** A method of determining the rate-law expression by carrying out a reaction with different initial concentrations and analyzing the resulting changes in initial rates, **621**, **624–626**, **656**
- Metric system**, **23–25**
- Meyer, Lothar**, **129**

- Micelle** A cluster of a large number of soap or detergent molecules or ions, assembled with their hydrophobic tails directed toward the center and their hydrophilic heads directed outward, **540**, **540f**, **543**
- Millikan, Robert**, 117–118, 119f
- Millimole** 1/1000 mole, **377**, **393**
- Mineral** A naturally occurring inorganic solid substance having a definite chemical composition and characteristic crystalline structure, **1018**, **1030**
- Miscibility** The ability of one liquid to mix with (dissolve in) another liquid, **510**–**511**, **510t**, **511f**, **543**
- Miscible liquids**, 450
- Mixture** A sample of matter composed of variable amounts of two or more substances, each of which retains its identity and properties, **13**–**14**, **13f**, **35**
Dalton's Law of Partial Pressures, 420–426, **421f**, **425f**
standard molar entropy and, 587
- Moderator** A substance such as hydrogen, deuterium, oxygen, or paraffin capable of slowing fast neutrons upon collision, **874**, **877**, **882**
- Molality (*m*)** Concentration expressed as number of moles of solute per kilogram of solvent, **515**–**516**, **543**
- Molar enthalpy of vaporization.** *see* **Molar heat of vaporization**
- Molar heat capacity** The amount of heat necessary to raise the temperature of one mole of a substance one degree Celsius with no change in state; usually expressed in kJ/mol · °C. *See* Specific heat, **465**, **495**
- Molar heat of condensation** The amount of heat that must be removed from one mole of a vapor at its condensation point to condense the vapor with no change in temperature; usually expressed in kJ/mol. *See* Heat of condensation, **495**
- Molar heat of fusion** The amount of heat required to melt one mole of a solid at its melting point with no change in temperature; usually expressed in kJ/mol. *See* Heat of fusion, **470**, **495**
- Molar heat of vaporization** The amount of heat required to vaporize one mole of a liquid at its boiling point with no change in temperature; usually expressed in kJ/mol. *See* Heat of vaporization, **465**, **495**
- Molarity (*M*)** The number of moles of solute per liter of solution, **99**–**101**, **106**, **393**
aqueous acid-base reactions, 376–380
- Molar mass** The mass, in grams, of one mole of a substance; numerically equal to the formula weight of the substance. *See* Formula weight; *see* Molecular weight, **52**, **73**
- Molar solubility** The number of moles of a solute that dissolve to produce a liter of saturated solution, **784**–**786**, **797**
- Mole** 6.022×10^{23} (Avogadro's number of) formula units (or molecules, for a molecular substance) of a substance. The mass, in grams, of one mole is numerically equal to the formula (molecular) weight of the substance, **51**–**56**, **59**, **73**, **810**
calculations based on chemical equations, **88**–**89**
- Molecular formula** A formula that indicates the actual number of atoms present in a molecule of a molecular substance. Compare with Simplest (empirical) formula, **61**, **73**
determination of, **65**–**67**
gases, **419**–**420**
- Molecular geometry** The arrangement of atoms (not electron groups) around a central atom of a molecule or polyatomic ion, **291**, **320**, **321t**, **322**
polar molecules, **292**–**293**, **293f**
- Molecular orbital (MO)** An orbital resulting from overlap and mixing of atomic orbitals on different atoms. An MO belongs to the molecule as a whole, **330**–**333**, **331**–**333f**, **343**
energy level diagrams, **333**–**334**, **334f**
- Molecular orbital theory** A theory of chemical bonding based on the postulated existence of molecular orbitals, **330**, **343**
- Molecular solids**, **488**, **488f**
- Molecular weight** The mass, in atomic mass units, of one molecule of a non-ionic (molecular) substance. Numerically equal to the mass, in grams, of one mole of such a substance. This number is obtained by adding the atomic weights of the atoms specified in the formula, **56**–**59**, **73**
determination by freezing point depression or boiling point elevation, **526**–**527**
gases, **419**–**420**
from osmotic pressure, **533**–**534**
- Molecule** The smallest particle of an element or compound that can have a stable independent existence, **6**, **35**. *see also*
Organic molecules
calculations based on chemical equations, **88**
Lewis formulas, **260**–**261**
mass of, **58**
polar, **292**–**293**, **293f**
- Mole fraction** The number of moles of a component of a mixture divided by the total number of moles in the mixture, **422**–**423**, **438**, **515**–**516**
- Mole fraction of a component in solution** The number of moles of the component divided by the total number of moles of all components, **543**
- Mole of reaction (mol rxn)** The amount of reaction that corresponds to the number of moles of each substance shown in the balanced equation, **598**
- Molten sodium chloride**, **806**–**807**, **806f**
- Molybdenum**, **1039**
- Monoatomic ion** An ion that consists of only one atom, **251**, **256**, **280**
- Monodentate** Describes ligands with only one donor atom, **994**, **1010**
- Monomers** The small molecules that are linked to form polymers, **943**, **982**
- Monoprotic acid** An acid that can form only one hydronium ion per molecule; may be strong or weak, **742**
- Monosaccharide** Simple sugars (monomers) from which more complex carbohydrates are constructed, **971**, **971f**, **982**
- Moseley, H. G. J.**, **121**–**122**, **122f**
- Myoglobin**, **976**
- Nanoscale**, **5**
- Nanotechnology**, **908**
- Native ore** A metal that occurs in an uncombined or free state in nature, **1017f**, **1018**, **1030**
- Natural radioactivity** Spontaneous decomposition of an atom, **163**
- Nearest neighbors**, **482**–**484**
- Negative deviation**, **521**
- Neon**, **125**, **125f**
- Neoprene**, **939**
- Nernst equation**, **827**–**832**
- Net ionic equation** An equation that results from canceling spectator ions from a total ionic equation, **216**, **240**, **359**, **367**, **388**–**389**
- Neutralization reaction** The reaction of an acid with a base to form a salt. Often, the reaction of hydrogen ions with hydroxide ions to form water molecules, **233**–**235**, **240**, **349**, **367**
in aqueous solutions, **358**–**361**
Arrhenius theory of, **349**–**350**
Brønsted-Lowry theory of, **350**–**353**, **351f**, **352f**
hydronium ion in, **350**
- Neutron** A subatomic nuclear particle having a mass of 1.0087 amu and no charge, **122**–**123**, **163**
bombardment, **873**–**874**
fast, **874**
–poor nuclei, **859**–**860**
–proton ratio, **853**, **854f**
–rich nuclei, **859**
slow, **874**
- Newlands, J. A. R.**, **175**
- Newton, Isaac**, **136f**
- Nickel-cadmium cell (NiCad battery)** A dry cell in which the anode is Cd, the cathode is NiO₂, and the electrolyte is basic, **840**, **842**
- Nickel sulfate**, **98**, **99f**
- Nitrates**, **1077**
- Nitric acid**, **418**, **732**, **1076**, **1077f**
- Nitrites**, **1077**
- Nitrobenzene**, **95**
- Nitrogen**, **336**, **1070**
amine complexes, **993**, **994t**
Haber process and, **686**–**688**, **687f**, **687t**
hydrogen compounds of, **1072**–**1073**, **1073f**
occurrence of, **1071**–**1072**, **1071t**, **1072f**
oxides, **1073**–**1074f**, **1073**–**1075**
oxides and photochemical smog, **1075**
oxoacids of, **1076**–**1077**, **1076**–**1077f**
properties of, **1071t**
- Nitrogen cycle** The complex series of reactions by which nitrogen is slowly but continually recycled in the atmosphere, lithosphere, and hydrosphere, **1080**
- Nitrogen dioxide**, **641**–**642**, **1074**
- Nitrogen oxide**, **339**–**340**, **339f**, **650**, **1073**–**1074**

- Nitrous acid, 210, 220, 263, 358, 1071, 1076, 1076f
- Nobel, Alfred, 935
- Noble gas configuration** The stable electron configuration of a noble gas, **201**
- Noble (rare) gases** Elements of Group 8A in the periodic table; formerly called inert gases, 133, **163, 174, 201, 240, 1080**
occurrence, uses, and properties, 1058–1059t
xenon compounds, 1059
- Nodal plane** A region in which the probability of finding an electron is zero; also known as a *node*, **331, 343**
- Nonbonding molecular orbital** A molecular orbital derived only from an atomic orbital of one atom; lends neither stability nor instability to a molecule or ion when populated with electrons, **343**
- Nonelectrolyte** Compounds that do not ionize (or dissociate into their constituent ions) when dissolved in water to produce aqueous solutions that will not conduct an electric current, **233–235, 240, 367, 710–711, 742**
- Nonideal gas behavior, 435
- Nonmetals** Elements above and to the right of the metalloids in the periodic table, 133, 133t, **163, 240**
oxides reactions with water, 195f, 197
reactions of oxygen with, 195–196, 196f
reactions with alkali metals, 252–254
reactions with alkaline earth metals, 255
- Nonpolar bond** A covalent bond between two atoms with the same electronegativity so that the electron density is symmetrically distributed, **276–278, 279, 280**
- Nonspontaneous change** A change for which the collection of reactants is more stable than the collection of products under the given conditions; also known as reactant-favored change, **578–579, 598**
- Nonvolatile acids, 365
- Normal boiling point** The temperature at which the vapor pressure of a liquid is equal to one atmosphere pressure, **464, 495, 523**
- Normal melting point** The melting (freezing) point at one atmosphere pressure, **469, 495**
- Normal oxide** A metal oxide containing the oxide ion, O^{2-} (oxygen in the -2 oxidation state), **194, 201**
- Normal salt** A salt that contains no ionizable H atoms or OH groups, **361, 367**
- Nuclear binding energy** The energy equivalent of the mass deficiency; energy released in the formation of an atom from subatomic particles. See *Binding energy*, **855, 882**
- Nuclear chemistry
artificial transmutations of elements, 871–874, 872–873f
decay series, 865, 866t
detection of radiation, 861–862, 862f
equations for nuclear reactions, 858–859
neutron-poor nuclei, 859–860
neutron-proton ratio and nuclear stability, 853, 854f
neutron-rich nuclei, 859
- nuclear fission, 874–876, 875–876f
nuclear fusion, 879–881, 879f, 881f
nuclear stability and binding energy, 854–857, 857f
nuclear waste management, 880
nuclei with atomic number greater than 83, 860–861
nucleus, 853
radioactive decay, 857, 858t
rates of decay and half-life, 863–864, 864–865f
uses of radionuclides, 865–871, 866f
- Nuclear fission** The process in which a heavy nucleus splits into nuclei of intermediated masses and one or more neutrons are emitted, **852, 874–876, 875–876f, 882**
reactors, 876–879, 876f
- Nuclear fusion** The combination of light nuclei to produce a heavier nucleus, **852, 879–881, 879f, 881f, 882**
- Nuclear reaction** A reaction involving a change in the composition of a nucleus; it can evolve or absorb an extraordinarily large amount of energy, **852, 882**
equations for, 858–859
- Nuclear reactor** A system in which controlled nuclear fission reactions generate heat energy on a large scale. The heat energy is subsequently converted into electrical energy, **882**
- Nuclear stability
binding energy and, 854–857, 857f
neutron-proton ratio and, 853, 854f
- Nuclear waste, 880
- Nucleic acid** A biopolymer consisting of repeating units of ribose or deoxyribose, phosphate, and selected bases, **978–981, 980–981f, 982**
- Nucleons** Particles comprising the nucleus; protons and neutrons, **853, 882**
- Nucleus** The very small, very dense, positively charged center of an atom, consisting of protons and neutrons (except for H, which has no neutrons), **121, 163, 853**
- Nuclides** Different atomic forms of all elements (in contrast to isotopes, which are different atomic forms of a single element), **882**
with atomic number greater than 83, 860–861
parent and daughter, 865
- Nuclide symbol** The symbol for an atom, E, in which, *E* is the symbol for an element, *Z* is its atomic number, and *A* is its mass number, **123, 163**
- Nylon, 941
- Octahedral** A term used to describe the electronic geometry around a central atom that has six electron groups. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to six atoms at the corners of an octahedron (AB_6), **322**
- Octahedral electronic geometry, 314–315
- Octane, 520
- Octet rule** Many representative elements attain at least a share of eight electrons in their valence shells when they form molecular or ionic compounds; this rule has some limitations, **261–267, 280, 295**
limitations, 269–274
- Oil** A liquid triester of glycerol and unsaturated fatty acids, **927–928, 944**
- Oil-drop experiment, 117, 119f
- Oligosaccharide** A molecule consisting of four to ten monosaccharides joined together by glycosidic bonds, **973, 973f, 982**
- Optical activity** The rotation of a plane of polarized light by chiral molecules, **957, 982, 1005, 1010**
- Optical isomers** Molecules that are nonsuperimposable mirror images of each other, that is, that bear the same relationship to each other as do left and right hands; also known as *enantiomers*, **956–959, 957–959f, 982, 1010**
coordination compounds, 1003–1005, 1004–1005f
- Orbital** Each allowed wave description of a stable state for an electron in an atom; a region of space in which the probability of finding an electron is high, **147, 151f–152f, 163**
- Order of a reactant** The power to which the reactant's concentration is raised in the rate-law expression, **656**
- Order of a reaction** The sum of the powers to which all concentrations are raised in the rate-law expression; also called the overall order of a reaction, **656**
- Ore** A natural deposit containing a mineral of an element to be extracted, **1017f, 1018, 1030**
pretreatment of, 1019–1020, 1019–1020f
- Organic chemistry** The study of carbon-containing compounds that contain C—C or C—H bonds and sometimes a few other elements such as oxygen, nitrogen, sulfur, phosphorus, and the halogens, **3, 888, 944. see also Functional group; Hydrocarbon**
addition reactions, 935–937
elimination reaction, 937–938, 937f
polymerization reactions, 938–942, 940t, 941–942f
substitution reactions, **932–935**
- Organic compounds, 44, Chapters 23 & 24
- Organic halides, 911–913, 912t
- Organic molecules. *see also Biopolymer*
combustion of, 967–968, 967t
conformations, 959–960, 959–960f
constitutional isomers, 954–955
oxidation-reduction reactions, 963–968, 967t
reactions of Brønsted-Lowry acids and bases, 960–963, 961–962t
- Osmosis** The process by which solvent molecules pass through a semipermeable membrane from a dilute solution into a more concentrated solution, **543**
reverse, 536–537
- Osmotic pressure** The hydrostatic pressure produced on the surface of a semipermeable membrane by osmosis, **531–535, 532f, 543**

- Ostwald process** An industrial process for the production of nitrogen oxide and nitric acid from ammonia and oxygen, **1076, 1080**
- Overlap of orbitals** The interaction of orbitals on different atoms in the same region of space, **322**
- Oxalic acid, **385–386**
- Oxidation** An increase in oxidation number; corresponds to a loss of electrons, **222, 240, 393**
- Oxidation numbers. *see* **Oxidation states (numbers)**
- Oxidation-reduction reaction** A reaction in which oxidation and reduction occur; also known as a *redox reaction*, **222–225, 239t, 240, 386, 393**
adding oxygen or hydrogen to complete, **388–390**
balancing, **387**
converting an ion to another species by, **795–796**
corrosion, **825–826f, 825–827**
organic molecules and, **963–968, 967t**
- Oxidation states (numbers)** Arbitrary numbers that can be used as aids in writing formulas and balancing equations; for single-atom ions, they correspond to the charge on the ion; less metallic elements are assigned negative oxidation states in compounds and ions, **187–189, 188t, 201**
transition metals, **1049–1050, 1050t**
- Oxidation** (as applied to organic compounds)
The increase of oxygen content or the decrease of hydrogen content of an organic molecule, **963–968, 967t, 982**
of alcohol, **965–966**
alkylbenzene, **966–967**
- Oxide** A binary compound of oxygen, **193–200, 195f, 196f, 197f, 201**
group 6A, **1068–1069, 1068f**
nitrogen, **1073–1074f, 1073–1075**
- Oxidizing agent** The substance that oxidizes another substance and is reduced, **240, 393**
- Oxoacid.** *see* **Ternary acid**
- Oxyanions, **1050–1051, 1051t**
- Oxygen, **12t, 126t**
atoms, **7, 7f**
balancing redox reactions and, **388–390**
chemical reactions and periodicity, **193–200**
corrosion and, **825–826f, 825–827**
oxidation state, **188**
reactions with nonmetals, **195–196, 196f**
- Ozone, **654–655**
- Paired electrons** Two electrons with opposite *m_s* values in the same orbital ($\uparrow\downarrow$) also known as *spin-paired electrons*, **152, 154, 163**
- Pairing energy** The energy required to pair two electrons in the same orbital, **1007, 1010**
- Paramagnetism** Attraction toward a magnetic field, stronger than diamagnetism, but still very weak compared with ferromagnetism; due to presence of unpaired electrons, **161–162, 162f, 163**
- Parent nuclide** A nuclide that undergoes nuclear decay, **865, 882**
- Partial neutralization, **762–763**
- Partial pressure** The pressure exerted by one gas in a mixture of gases, **420–426, 438, 691–692**
- Particulate matter** Finely divided solid particles suspended in air, **1080**
- Pascal (Pa)** The SI unit of pressure; it is defined as the pressure exerted by a force of one newton acting on an area of one square meter, **405, 438**
- Pauli Exclusion Principle** No two electrons in the same atom may have identical sets of four quantum numbers, **154, 163, 333**
- Peptide bond** A bond formed by elimination of a molecule of water between the amino group of one amino acid and the carboxylic acid group of another, **942, 944, 974–975, 982**
- Peptides** Compounds formed by the linking of small numbers of amino acids, **974–976, 976t, 977f, 982**
- Percentage, **26, 29**
- Percent by mass** 100% multiplied by the mass of a solute divided by the mass of the solution in which it is contained, **98, 106**
- Percent composition** The mass percentage of each element in a compound, **60–61, 73**
- Percent ionization of weak electrolytes**
The percent of the weak electrolyte that ionized in a solution of a given concentration, **543, 722–723**
- Percent purity** The mass percentage of a specified compound or element in an impure sample, **71, 73**
- Percent yield** 100% times actual yield divided by theoretical yield, **95, 106**
sequential reactions, **97**
- Perchloric acid, **198f, 1065**
- Period** The elements in a horizontal row of the periodic table, **132, 163**
- Periodicity** Regular periodic variations of properties of elements with atomic number (and position in the periodic table), **163, 201**
hydrogen and hydrides, **190–193**
- Periodic law** The properties of the elements are periodic functions of their atomic numbers, **132, 163, 174, 201**
- Periodic table** An arrangement of elements in order of increasing atomic number that also emphasizes periodicity, **129–134, 130f, 132t, 163, 174–176**
electron configurations and, **159–161, 160f, 161f**
Mendeleev's design, **129–132**
- Peroxide** A compound containing oxygen in the -1 oxidation state. Metal peroxides contain the peroxide ion, O_2^{2-} , **194, 201**
- Peroxyacyl nitrates (PANs)** Photochemically produced oxidizing agents capable of causing damage to plants and animals, **1075, 1080**
- Petroleum, **900**
- pH** The negative logarithm of the concentration (mol/L) of the H_3O^+ (or H^+) ion; the commonly used scale ranges from -1 to 15, **713–716, 717f, 742**
buffer solution, **759–760**
- Phase changes**
dipole-dipole interactions, **453–454, 454f**
dispersion forces, **456–458, 457f, 458t**
hydrogen bonding, **454–455, 455f**
and intermolecular attractions, **451–458, 452f**
ion-ion interactions, **453, 453t**
standard molar entropy and, **584**
- Phase diagram** A diagram that shows equilibrium temperature-pressure relationships for different phases of a substance, **472–475, 473–475f, 495**
- Phenol** A hydrocarbon derivative that contains an -OH group bound to an aromatic ring, **913–918, 913f, 917f, 917t, 944**
reactions, **962**
- Pheromones, **964**
- pH meter** A device to measure the pH of a solution; typically consists of a pH-dependent glass electrode and a reference electrode (often a saturated calomel electrode), **833, 833f, 842**
- Phosphoric acid, **197, 210, 220f, 233, 361–362, 365–366, 729, 1070**
- Phosphorus, **7f, 619, 1077–1078, 1077–1078f**
discovery of, **175**
properties of, **1071t**
- Phosphorus pentafluoride, **272**
- Phosphorus trihalides, **366**
- Photochemical smog** A brownish smog occurring in urban areas that receive large amounts of sunlight; caused by photochemical (light-induced) reactions among nitrogen oxides, hydrocarbons, and other components of polluted air that produce photochemical oxidants, **1075, 1080**
- Photoelectric effect** Emission of an electron from the surface of a metal, caused by impinging electromagnetic radiation of certain minimum energy; the resulting current increases with increasing intensity of radiation, **138, 138f, 163**
- Photographic detection of radiation, **861**
- Photon** A subatomic particle having a mass of 1.0073 amu and a charge of $1+$, found in the nuclei of atoms, **137, 163**
- Physical change** A change in which a substance changes from one physical state to another, but no substances with different compositions are formed, **12–13, 13f, 35**
- Physical chemistry
defined, **3**
- Physical property.** *see* **properties**
- Pi (π) bond** A bond resulting from the side-on overlap of atomic orbitals, in which the regions of electron sharing are on opposite sides of and parallel to an imaginary line connecting the bonded atoms; a bond resulting from electron occupancy of a pi molecular orbital, **317–319, 322, 343, 944**
- Pig iron** The iron obtained from the blast furnace, **1027, 1030**
- Pigments, **924**

- Pi (π) molecular orbital** A molecular orbital resulting from side-on overlap of atomic orbitals, **332, 344**
- pK_a** The negative logarithm of K_a , the ionization constant for a weak acid, **742**
- pK_b** The negative logarithm of the ion product for water, **742**
- Planck's constant, **137, 142**
- Plane-polarized light** Light waves in which all the electric vectors are oscillating in one plane, **1010**
- Plasma** A physical state of matter that exists at extremely high temperatures, in which all molecules are dissociated and most atoms are ionized, **882**
- Platinum, **992–993**
- pOH** The negative logarithm of the concentration (mol/L) of the OH^- ion; the commonly used scale ranges from 15 to -1 , **742**
- Polar bond** A covalent bond between two atoms with different electronegativities so that the electron density is unsymmetrically distributed, **276–278, 279, 280**
- Polarimeter** A device used to measure optical activity, **958f, 1005f, 1010**
- Polarizability. *see* **Dispersion forces**
- Polarization of an electrode** Buildup of a product of oxidation or reduction at an electrode, preventing further reaction, **837, 842**
- Polar molecules, **292–293, 293f**
- Polonium, **480, 483, 853, 871**
- Polyamide** A polymeric amide, **941, 944**
- Polyatomic ion** Consisting of more than one atom. Elements such as Cl_2 , P_4 , and S_8 exist as polyatomic molecules. Examples of polyatomic ions are the ammonium ion, NH_4^+ , and the sulfate ion, SO_4^{2-} , **48, 73, 251, 280**
- Lewis formulas, **260–261**
- Polydentate** Describes ligands with more than one donor atom, **996, 1010**
- Polyene** A compound that contains more than one double bond per molecule, **944**
- Polyesters**, **940**
- Polyethylene, **938**
- Polymerization** The combination of many small molecules (monomers) to form large molecules (polymers), **938–942, 940t, 941–942f, 944, 982**
- condensation, **940–942, 941–942f**
- Polymers** Large molecules formed by the combination of many small molecules (monomers), **938, 944, 982**
- Polymorphous** Refers to substances that crystallize in more than one crystalline arrangement, **480, 495**
- Polyol** An alcohol that contains more than one —OH group; a polyol with two —OH groups is called a glycol, **916–917, 916f, 944**
- Polypeptide** A polymer composed of amino acids linked by peptide bonds, **942, 944, 974–977, 976t, 977f, 982**
- Polyprotic acid** An acid that contains more than one ionizable hydrogen atom per formula unit, **367, 729–732, 731t, 742**
- Polysaccharide** Carbohydrates that contain more than ten monosaccharide units, **973, 973f, 982**
- p orbitals** Beginning with the second shell, a set of three degenerate, mutually perpendicular, equal-arm, dumbbell-shaped atomic orbitals per shell, **151f, 155, 163**
- Positional isomers, **893**
- Positive deviation, **520–521**
- Positron** A nuclear particle with the mass of an electron but opposite charge, **882**
- Positron emission**
- tomography (PET) (*see* **Electron capture**)
- Positron emission tomography (PET), **870**
- Post-transition metal** Representative metals in the “ p block,” **1036, 1045, 1053. *see also* d -Transition elements (metals)**
- periodic trends, **1045–1048, 1045t, 1046f**
- Potassium, **1041f, 1042**
- Potassium chlorate, **68**
- Potassium permanganate, **100, 100f, 375f, 388–389, 388f, 391, 391f**
- Potential energy** Energy that matter possesses by virtue of its position, condition, or composition, **4, 35, 553, 554f, 598**
- Precipitate** An insoluble solid that forms and separates from a solution, **235, 240, 787–788, 797**
- dissolution of, **795–796**
- Precipitation reaction** A reaction in which a solid (precipitate) forms, **235–237, 240, 788–789**
- fractional, **790–792**
- Precision** How closely repeated measurements of the same quantity agree with one another, **35**
- Pressure** Force per unit area, **403–405, 403f–405f, 438**
- Boyle's law and, **405–410, 408f**
- chemical equilibrium and, **682–683**
- effect on solubility, **515, 515f**
- First Law of Thermodynamics and, **572–574, 573f**
- osmotic, **531–535, 532f**
- phase diagrams, **472–475, 473–475f**
- volume relationship, **405–410, 408f**
- Pressure-volume work** Work done by a gas when it expands against an external pressure, or work done on a system as gases are compressed or consumed in the presence of an external pressure, **598**
- Pretreatment of ores, **1019–1020, 1019–1020f**
- Primary alcohol** An alcohol with no or one R group bonded to the carbon bearing the —OH group, **914, 917t, 944**
- Primary amine** An amine in which one H atom of ammonia has been replaced by an organic group, **921–922, 922f, 944**
- Primary standard** A substance of a known high degree of purity that undergoes one invariable reaction with the other reactant of interest, **381, 382, 393**
- Primary structure** The sequence of the monomeric units in proteins, carbohydrates, and so on, **975, 982**
- Primary voltaic cell** A voltaic cell that cannot be recharged; no further chemical reaction is possible once the reactants are consumed, **836–838, 837–838f, 842**
- Principal quantum number, **148**
- Product-favored change. *see* Spontaneous change**
- Products** Substances produced in a chemical reaction, **82, 106**
- Propane, **613f**
- Properties** Characteristics that describe samples of matter. Chemical properties are exhibited as matter undergoes chemical changes. Physical properties are exhibited by matter with no changes in chemical composition, **10, 12f, 12t, 16, 35**
- Properties, physical. *see* **properties**
- Protein** A naturally occurring polymeric chain of L-amino acids linked together by peptide bonds, **942, 944, 975–977, 982**
- amino acids found in, **976t, 977f**
- functions of, **977, 978t**
- Protic acid** An Arrhenius acid, or a Brønsted-Lowry acid, **349, 367**
- Proton** A subatomic particle having a mass of 1.0073 amu and a charge of 11, found in the nuclei of atoms, **119**
- —neutron ratio , **853, 854f**
- Pure substance, **14**
- Q , reaction quotient**, The mass action expression under any set of conditions (not necessarily equilibrium); its magnitude relative to K determines the direction in which a reaction must occur to establish equilibrium, **674–676, 700**
- quantum** A “packet” of energy. *See* Photon, **137, 163**
- quantum mechanics** A mathematical method of treating particles on the basis of quantum theory, which assumes that energy (of small particles) is not infinitely divisible, **146–147, 147f, 163**
- quantum numbers** Numbers that describe the energies of electrons in atoms; they are derived from quantum mechanical treatment, **147–148, 149t, 158, 163**
- quartz, **489, 489f**
- quaternary structure, **976**
- Racemic mixture** A single sample containing equal amounts of the two enantiomers (optical isomers) of a compound; does not rotate the plane of polarized light, **957, 982, 1005, 1010**
- Radiant energy. *see* **Electromagnetic radiation**
- Radiation** High-energy particles or rays emitted in nuclear decay processes, **857, 858t, 882**
- detection of, **861–862, 862f**
- Radical** A species containing one or more unpaired electrons many radicals are very reactive, **193, 201, 1080**
- Radioactive dating** A method of dating ancient objects by determining the ratio of amounts of a parent nuclide and one of its decay products present in an object and relating the ratio to the object's age via half-life calculations, **865–868, 882**

Radioactive decay, 857, 858t, 860–861
household radon exposure and lung cancer, 869
rates of decay and half-life, 863–864, 864–865f
series, 865, 866t

Radioactive tracer A small amount of radioisotope that replaces a nonradioactive isotope of the element in a compound whose path (e.g., in the body) or whose decomposition products are to be monitored by detection of radioactivity; also known as a *radiopharmaceutical*, 868–870, 870f, 871, 882

Radioactivity The spontaneous disintegration of atomic nuclei, 852, 882

Radioisotope A radioactive isotope of an element, 852, 882

Radionuclide A radioactive nuclide, 882
rates of decay and half-life, 863–864, 864–865f
uses of, 865–871, 866f

Radon, 869, 1058

Ramsay, William, 18

Raoult's Law The vapor pressure of a solvent in an ideal solution is directly proportional to the mole fraction of the solvent in the solution, 518–519f, 518–521, 521f, 543

Rate constant An experimentally determined proportionality constant that is different for different reactions and that, for a given reaction, changes only with temperature or the presence of a catalyst; k in the rate-law expression, $\text{rate} = k[A]^x[B]^y$; also known as the *specific rate constant*, 620, 656

Rate-determining step The slowest elementary step in a reaction mechanism; the step that limits the overall rate of reaction, 641, 656

Rate-law expression An equation that relates the rate of a reaction to the concentrations of the reactants and the specific rate constant; $\text{rate} = k[A]^x[B]^y$. The exponents of reactant concentrations *do not necessarily* match the coefficients in the overall balanced chemical equation. The rate-law expression must be determined from experimental data; also known as the *rate law*, 619–626, 632t, 656
reaction mechanisms and, 640–643

Rate of reaction The change in concentration of a reactant or product per unit time, 612, 613–618, 614f, 616t, 617f, 656

Rayleigh, Baron, 18

Reactant-favored change. *see*

Nonspontaneous change

Reactants Substances consumed in a chemical reaction, 82, 106

concentrations of, 619–626

reaction rate and nature of, 619

Reaction coordinate The progress along the potential energy pathway from reactants to products, 639f, 656

Reaction intermediate A species that is produced and then entirely consumed during a multistep reaction; usually short-lived, 656

Reaction mechanism The sequence of fundamental steps by which reactants are converted into products, 640–643, 656

Reaction quotient (Q) The mass action expression under any set of conditions (not necessarily equilibrium); its magnitude relative to K determines the direction in which reaction must occur to establish equilibrium, 674–676, 700, 787, 797

Reaction rate. *see* **Rate of reaction**

Reaction ratio The relative amounts of reactants and products involved in a reaction; may be the ratio of moles, or masses. Also called *Stoichiometric ratio*, 106, 376, 378

Reaction stoichiometry Description of the quantitative relationships among substances as they participate in chemical reactions, 44, 82, 106

Reagent. *see* **limiting reactant (or reagent)**

Red blood cells, 989f

Redox reaction An oxidation-reduction reaction, 393. *see also* **Oxidation-reduction reaction**

balancing, 387

titrations calculations, 390–393

Reducing agent The substance that reduces another substance and is oxidized, 223, 240, 393

Reduction A decrease in oxidation number; corresponds to a gain of electrons, 222, 240, 393

Reduction (as applied to organic compounds) The decrease of oxygen content or the increase of hydrogen content of an organic molecule, 963–968, 967t, 982

Refining Purifying of a substance, 1022, 1023f, 1030

Relationship between ΔH and ΔE , 577–578

Representative elements The A group elements in the periodic table, 174, 202, 1036

Resonance A concept in which two or more Lewis formulas for the same arrangement of atoms (resonance structures) are used to describe the bonding in a molecule or ion, 274–275, 280

Reverse osmosis The forced flow of solvent molecules through a semipermeable membrane from a concentrated solution into a dilute solution. This is accomplished by application of hydrostatic pressure on the concentrated side greater than the osmotic pressure that is opposing it, 536–537, 543

Reversible reaction A reaction that occurs in both directions; described with double arrows ($\rightleftharpoons$). The equal-length arrows do not indicate equal amounts of reactants and products, just that some of each are present. Chemists sometimes indicate the favored direction of a reversible reaction by using a longer arrow on top or bottom, 211–212, 213t, 240, 668, 700

Ribose The carbohydrate found in RNA, 982

RNA Ribonucleic acid; a nucleic acid consisting of phosphate, ribose, and the four bases adenine, cytosine, guanine, and uracil, 978–981, 980–981f, 982

Roasting Heating an ore of an element in the presence of air, 200, 202, 1020, 1020f, 1030

Rock candy, 43f

Root-mean-square speed The square root of the mean-square speed. This is equal to

$\sqrt{\frac{3RT}{m}}$ for an ideal gas. The root-mean-square speed is slightly different from the average speed, but the two quantities are proportional, 433, 438

Rubber, 938

Rutherford, Ernest, 119, 120–121, 120f, 852, 853

Rydberg, Johannes, 139

Sacrificial anode A more active metal that is attached to a less active metal protect the less active metal cathode against corrosion, 842

Salt An ionic compound that contains a cation other than H^+ and an anion other than OH^- or O^{2-} , 208, 240, 367

acidic and basic, 361–362, 362f

buffer solutions and, 750–756, 752t, 760–761
containing small, highly charged cations, 740–741

and oxoacids of nitrogen, 1076–1077, 1076–1077f

strong bases and strong acids, 733

strong bases and weak acids, 733–736

taming dangerous acids with harmless, 738
ternary acid, 360

weak bases and strong acids, 736–737

weak bases and weak acids, 737–740

Salt bridge A U-shaped tube containing an electrolyte that connects two half-cells of a voltaic cell, 812, 842

Saponification The hydrolysis of esters in the presence of strong bases, 969–970, 970f, 982

Saturated calomel electrode An electrode that consists of a platinum wire in contact with a paste of liquid mercury and solid mercury(I) chloride, $Hg_2Cl_2(s)$, all immersed in a saturated solution of potassium chloride, KCl ; often used as the reference electrode in a pH meter, 833, 833f, 842

Saturated hydrocarbons Hydrocarbons that contain only single bonds; also known as *alkanes* or *paraffin hydrocarbons*, 890, 944.

see also **Hydrocarbon**

alkanes and cycloalkanes, 890–895, 891–895f, 893–894t

naming, 895–899, 896t

Saturated solution A solution in which no more solute will dissolve at a given temperature, 513, 543

Schrödinger equation, 147, 153, 330

Scientific (natural) law A general statement based on the observed behavior of matter, to which no exceptions are known, 4, 35

- Scintillation counter** A device used for the quantitative detection of radiation, **861, 882**
- Secondary alcohol** An alcohol with two R groups bonded to the carbon bearing the —OH group, **914, 944**
- Secondary amine** An amine in which the two H atoms of ammonia have been replaced by organic groups, **921–922, 922f, 944**
- Secondary standard** A solution that has been titrated against a primary standard. A standard solution is a secondary standard, **381, 393**
- Secondary voltaic cell** A voltaic cell that can be recharged; the original reactants can be regenerated by reversing the direction of current flow, **838–841, 839f, 841f, 842**
- Second Law of Thermodynamics** The universe tends toward a state of greater disorder in spontaneous processes, **589–591, 591t, 598**
- Second-order reactions, **629–631, 630f, 632**
- Seesaw** A term used to describe the molecular geometry of a molecule or polyatomic ion that has four atoms bonded to a central atom and one lone pair on the central atom (AB₄U), **322**
- Selenium, **1039**
- occurrence, properties, and uses, **1066, 1066t**
- Semiconductor** A substance that does not conduct electricity at low temperatures but does so at higher temperatures, **134, 240, 491, 491f, 492–493, 495**
- Semipermeable membrane** A thin partition between two solutions through which certain molecules can pass but others cannot, **531, 532f, 543**
- Sequential reaction** A chemical process in which several reaction steps are required to convert starting materials into products, **96–97, 106**
- Shielding, light water reactor, **878**
- Shielding effect** Electrons in filled *sets* of *s* and *p* orbitals between the nucleus and outer shell electrons shield the outer shell electrons somewhat from the effect of protons in the nucleus; also called screening effect, **177, 202**
- Sigma (σ) bond** A bond resulting from the head-on overlap of atomic orbitals, in which the region of electron sharing along and (cylindrically) symmetrical to an imaginary line connecting the bonded atoms, **317–319, 322, 344, 944**
- Sigma (σ) molecular orbital** A molecular orbital resulting from head-on overlap of two atomic orbitals, **331, 344**
- Significant figures** Digits that indicate the precision of measurements—digits of a measured number that have uncertainty only in the last digit, **35**
- Silicates, **1078–1079, 1079f**
- Silicon, **133f, 1078–1079, 1079f**
- Silver chloride, **784**
- Silver chromate, **783**
- Silver-copper cell, **815–816, 816f**
- Simplest formula** The smallest whole-number ratio of atoms present in a compound; also called empirical formula. Compare with molecular formula, **61–65, 73**
- Simultaneous equilibria, **792–794**
- Single bond** A covalent bond resulting from the sharing of two electrons (one pair) between two atoms, **259, 259f, 280**
- SI units, **19, 19t, 21t, 23–24**
- for the mole, **51**
- Slag** Unwanted material produced during smelting, **1030**
- Slow neutron** A fast neutron slowed by collision with a moderator, **874, 882**
- Smelting** Chemical reduction of a metal from its ore by treating the molten ore with a reducing agent, **1030**
- Soap** An emulsifier that can disperse nonpolar substances in water; the sodium salt of a long-chain organic acid; consists of a long hydrocarbon chain attached to a carboxylate group, —CO₂—Na⁺; the alkali metal (Na or K) salt of a long-chain fatty acid, **543, 970, 970f, 982**
- Sodium, **16f, 1041, 1041f**
- atomic radii, **177**
- Sodium acetate, **756–757**
- Sodium bicarbonate, **347**
- Sodium carbonate, **382, 382f**
- Sodium chloride, **48, 48f, 254, 254f, 348**
- associated ions, **528**
- dissolution, **507, 509–510, 509f**
- electrolysis of aqueous, **807, 807f**
- electrolysis of molten, **806–807, 806f**
- ionic bonding in, **256–257, 486, 486f**
- molecular weight, **57**
- van't Hoff factor, **529**
- Sodium hydrogen carbonate, **362, 362f**
- Sodium hydroxide, **57, 98f, 348, 385**
- Sodium sulfate, **808, 808f**
- Sol** A colloidal dispersion of a solid in a liquid, **536–537, 543**
- Solar energy, **851**
- Solid aerosol** A colloidal dispersion of a solid in a gas, **543**
- Solid emulsion** A colloidal dispersion of a liquid in a solid, **543**
- Solid foam** A colloidal dispersion of a gas in a solid, **543**
- Solidification, **451**
- Solids, **9, 10f**
- amorphous, **475–477, 478f**
- bonding in, **481–482f, 481–489, 481t, 486–489f**
- covalent, **488–489, 489f**
- crystalline, **475–477, 478f**
- dissolution in liquids, **508–510, 509f**
- heat transfer involving, **469–472, 470f, 470t**
- intermolecular attractions and phase changes, **451–458, 452f, 453t, 454–456f, 457t**
- ionic, **486–488, 486–488f**
- kinetic-molecular description of, **450–451, 451f**
- melting point, **469**
- metallic, **481–482f, 481–486, 481t, 486f**
- molecular, **488, 488f**
- phase diagrams, **472–475, 473–475f**
- structures of crystal, **478–480, 478t, 479–480f**
- sublimation and vapor pressure of, **472, 472f**
- Solid sol** A colloidal dispersion of a solid in a solid, **543**
- Solubility product constant (K_{sp})** The equilibrium constant that applies to the dissolution of a slightly soluble compound, **780–782, 781f, 797**
- determination of, **782–784**
- uses of, **784–789**
- Solubility product principle** The solubility product constant expression for a slightly soluble compound is the product of the concentrations of the constituent ions, each raised to the power that corresponds to the number of ions in one formula unit, **797**
- Solute** The dispersed (dissolved) phase of a solution, **97, 103–104, 106, 506**
- mass of, **99, 100–101**
- percent of, **98, 99**
- Solution** A homogeneous mixture of two or more substances, **13, 97, 106, 506. see also Aqueous solution**
- adsorption phenomenon, **535–537, 538f, 538t**
- boiling point elevation, **523–524, 524t**
- buffer, **750–756, 752t**
- concentration of, **97–101**
- determination of molecular weight by
- freezing point depression or boiling point elevation, **526–527**
 - dilution of, **102–103**
- dissolution effect of pressure on solubility, **515, 515f**
- dissolution effect of temperature on solubility, **514–515, 514f**
- dissolution of gases in liquids, **512–513, 512f**
- dissolution of liquids in liquids, **510–511, 510t, 511f**
- dissolution of solids in liquids, **508–510, 509f**
- dissolution rates of saturation and, **513**
- dissolution spontaneity, **506–508, 507f**
- fractional distillation, **522–523, 522–523f**
- freezing point depression, **525–526**
- hydrophilic and hydrophobic colloids, **539–540f, 539–541**
- molality and mole fraction, **516–517**
- molarity, **99–101, 376–380**
- osmotic pressure, **531–535, 532f**
- Raoult's Law, **518–519f, 518–521, 521f**
- simultaneous equilibria, **792–794**
- spontaneity of dissolution process and, **506–508, 507f**
- Tyndall effect, **535**
- used in chemical reactions, **103–105**
- Solvation** The process by which solvent molecules surround and interact with solute ions or molecules, **508, 543**
- Solvent** The dispersing medium of a solution, **97, 106, 524, 914–915**
- Solvolysis** The reaction of a substance with the solvent with the solvent in which it is dissolved, **732–733, 742**
- SO₂–O₂–SO₃ system, **669, 670f**
- s orbital** A spherically symmetrical atomic orbital; one per shell, **150f, 151f, 163**
- Space-filling model, **45, 46f, 287f**
- Specific gravity** The ratio of the density of a substance to the density of water at the same temperature, **28–29**

- Specific heat** The amount of heat required to raise the temperature of one gram of a substance by one degree Celsius with no change in state; usually expressed in J/g • °C. See Molar heat capacity, 31–34, 35, 465, 495
- Spectator ions** Ions that appear in solution on both sides of the total ionic equation; they undergo no change in the chemical reaction, 216, 240, 367
- Spectral color** The color associated with the wavelengths of light that are absorbed, 1008–1009, 1011
- Spectral line** Any of a number of lines corresponding to definite wavelengths in an atomic emission or absorption spectrum; these lines represent the energy difference between two energy levels, 163
- Spectrochemical series** An arrangement of ligands in order of increasing ligand field strength, 1009, 1011
- Spectrum** Display of component wavelengths of electromagnetic radiation, 163
- Spin quantum number (m_s)** The quantum mechanical solution to a wave equation that indicates the relative spins of electrons (“spin up” and “spin down”), 148, 152f, 163
- Spontaneous change** A change for which the collection of products is more stable than the collection of reactants under the given conditions; also known as *product-favored change*, 578–579, 598
two aspects of, 579–580, 579f
- Square planar** A term used to describe molecules and polyatomic ions that have one atom in the center and four atoms at the corners of a square, 322
- Square planar complex** A complex in which the metal atom or ion is in the center of a square plane, with a ligand donor atom at each of the four corners, 1011
- Square pyramidal** A term used to describe the molecular geometry of a molecule or polyatomic ion that has five atoms bonded to a central atom and one lone pair on the central atom (AB₅U), 322
- Stable isotopes, 127
- Standard cell** A cell in which all reactants and products are in their thermodynamic standard states (1 M for solution species and 1 atm partial pressure for gases), 842
- Standard cell potential** The potential difference, E°_{cell} , between standard reduction and oxidation half-cells, 842
relationship between standard cell potential and, 835–836
- Standard electrochemical conditions** 1 M concentration for solution species, 1 atm partial pressure for gases, and pure solids and liquids, 842
- Standard electrode** A half-cell in which the oxidized and reduced forms of a species are present at unit activity: 1 M solutions of dissolved species, 1 atm partial pressure of gases, and pure solids and liquids, 842
- Standard electrode potential** By convention, the potential (E°) of a half-reaction as a reduction relative to the standard hydrogen electrode, when all species are present at unit activity, 816–817, 819–820, 821t, 842
copper-SHE cell, 818–819, 819f
effect of concentrations on, 827–836, 833–834f
Nernst equation, 827–832
for other half-reactions, 823–825, 823t
standard hydrogen electrode, 817, 817f
uses of, 821–822
zinc-SHE cell, 817–818, 818f
- Standard enthalpy change (ΔH°)** The enthalpy change in which the number of moles of reactant specified in the balanced chemical equation, all at standard states, is converted completely to the specified number of moles of products, all at standard states, 561–562, 598
- Standard entropy change (ΔS°)** The entropy change in which the number of moles of reactants specified in the balanced chemical equation, all at standard states, is converted completely to the specified number of moles of products, all at standard states, 599
- Standard Gibbs free energy change (ΔG°)** The indicator of spontaneity of a process at constant T and P . If ΔG° is negative, the process is product-favored (spontaneous); if ΔG° is positive, the reverse process is reactant-favored (nonspontaneous), 599
- Standard hydrogen electrode (SHE)** An electrode consisting of a platinum electrode that is immersed in a 1 M H⁺ solution and that has H₂ gas bubbled over it at 1 atm pressure; defined as the reference electrode, with a potential of *exactly* 0.0000 . . . volts, 817, 817f, 842–843
- Standardization** The process by which the concentration of a solution is accurately determined by titrating it against an accurately known amount of a primary standard, 381, 393
- Standard molar enthalpy of formation (ΔH_f°) (of a substance)** The enthalpy change for the formation of one mole of a substance in a specified state from its elements in their standard states; also known as *standard molar heat of formation* or *just heat of formation*, 562–563, 563t, 599
- Standard molar entropy (S°) (of a substance)** The absolute entropy of a substance in its standard state at 298 K, 583, 598
- Standard molar heat of formation.** *see* Standard molar enthalpy of formation
- Standard molar volume** The volume occupied by one mole of an ideal gas under standard conditions, 22.414 liters, 414–415, 414t, 438
- Standard temperature and pressure (STP)** Standard temperature 0°C (273.15 K), and standard pressure, one atmosphere, are standard conditions for gases, 412, 438
- Standing wave, 146
- State function** A variable that defines the state of a system; a function that is independent of the pathway by which a process occurs, 555, 598
- States of matter, 9–10, 10f, 402, 450–451, 451f
- Steel** Iron alloyed with other metals, such as Mn, Cr, Ni, W, Mo, and V, and sometimes with C and Si, 1027, 1027t, 1030
- Stereochemistry** The study of the three-dimensional aspects of molecular structure, 982
- Stereoisomers** Isomers in which the atoms are linked together in the same atom-to-atom order, but with different arrangements in space. *See* Geometric isomers; Optical isomers, 955–959, 956–959f, 982, 1011
coordination compounds, 1000–1005, 1002f, 1004–1005f
- Stoichiometric ratio.** *see* reaction ratio
- Stoichiometry** Description of the quantitative relationships among elements in compounds (composition stoichiometry) and among substances as they undergo chemical changes (reaction stoichiometry), 44, 73, 106
solution, 104–105
- Stoney, George, 117
- Strong acid** An acid that ionizes (separates into ions) completely, or very nearly completely, in dilute aqueous solution, 209–211, 211f, 211t, 212f, 240, 359. *see also* Acid
polyprotic, 729–732, 731t
salts of strong bases and, 733
salts of weak bases and, 736–737
salts that contain small, highly charged cations, 740–741, 740f
solvolyis, 732–733
titration curves, 765–768, 766t, 767f, 767t
- Strong base** Metal hydroxide that is soluble in water and dissociates completely in dilute aqueous solution, 212, 213t, 240, 358–359. *see also* Base
salts, 733–736
titration curves, 765–769, 766t, 767f, 767t, 769t, 770f
- Strong electrolyte** Compounds that ionize (or dissociate into their constituent ions) completely, or nearly completely, when dissolved in water to produce aqueous solutions that conduct an electric current, 240, 710–711, 710t, 742. *see also* Electrolyte
- Strong field ligand** A ligand that exerts a strong crystal or ligand electric field and generally forms low spin complexes with metal ions when possible. A ligand that forms a strong dative bond, 1011
- Strontium, 1044
- Strontium-90, 863–864, 864f
- Structural formula** A representation that shows how atoms are connected in a compound, 45, 46f, 73
- Structural (constitutional) isomers** (Applied to coordination compounds.) Isomers whose differences involve more than a single coordination sphere or else different donor atoms; they include ionization isomers, hydrate isomers, coordination isomers, and linkage isomers, 999–1000, 1011
- Structural isomers.** *see* Constitutional isomers

Subatomic particles. *see* **Fundamental particles**

Sublimation The direct vaporization of a solid by heating without passing through the liquid state, 11f, **472**, 472f, **495**

Substance Any kind of matter all specimens of which have the same chemical composition and physical properties, **14**, **35**

Substitution reaction A reaction in which an atom or group of atoms attached to a carbon atom is replaced by another atom or group of atoms. No change occurs in the degree of saturation at the reactive carbon, **932–935**, **944**, 968–969

Substrate A reactant in an enzyme-catalyzed reaction, **653**, **656**

Sucrose, 43, 43f, 519, 524, 525–526

Sulfur, 7f, 14f, 17f, 197f, 1067f
occurrence, properties, and uses, 1065–1066, 1066t

oxoacids of, 1069–1070, 1070f

Sulfur dioxide, 69, 650, 669, 670f, 1068, 1068f

Sulfuric acid, 101, 104, 366, 385, 1070, 1070f
dissolution, 511, 511f

Sulfur tetrafluoride, 273, 287f, 312–313

Sulfur trioxide, 651, 669, 670f, 1069

Supercritical fluid A substance at a temperature above its critical temperature. A supercritical fluid cannot be described as either a liquid or gas, but has the properties of both, **474**, **495**

Superoxide A compound containing the superoxide ion, O_2^- (oxygen in the $-1/2$ oxidation state), **194**, **202**

Supersaturated solution A (metastable) solution that contains a higher-than-saturation concentration of solute; slight disturbance or seeding causes crystallization of excess solute, **513**, **543**

Surface tension The result of inward intermolecular forces of attraction among liquid particles that must be overcome to expand the surface area, **460**, 460f, **495**

Surfactant A “surface-active agent”; a substance that has the ability to emulsify and wash away oil and grease in an aqueous suspension, **541**, **543**

Surroundings Everything in the environment of the system, **555**, **598**

Symbol (of an element) A letter or group of letters that represents (identifies) an element, **16**, **35**
common element, 17t

System The substances of interest in a process; the part of the universe under investigation, **555**, **598**

t_{2g} orbitals A set of d_{xy} , d_{yz} , and d_{zx} orbitals in an octahedral complex; those d orbitals within a set with lobes bisecting (midway between) the x , y , and z axes, **1006**, **1011**

Tellurium, 1066, 1066t

Temperature A measure of the intensity of heat, that is, the hotness or coldness of a sample or object, **29–31**, **35**, 468
Arrhenius equation, 643–647, 644–646f
Boyle’s law and, 405–410, 408f
Charles’ law and, 410–412, 411f

chemical equilibrium and, 684

effect on solubility, 514–515, 514f

evaluation of equilibrium constants at different, 699

phase diagrams, 472–475, 473–475f

standard molar entropy and, 585–586

standard temperature and pressure, 412

Ternary acid An acid containing three elements: H, O, and (usually) another nonmetal, **197**, **202**, **219–221**, 220t, **240**, 357–358, 366, **367**, 1064–1065, 1065t
everyday salts of, 360
of nitrogen and their salts, 1076–1077, 1076–1077f
of sulfur, 1069–1070, 1070f

Ternary compound A compound consisting of three elements; may be ionic or molecular, **219–221**, 220t, **240**, **367**

Tertiary alcohol An alcohol with three R groups bonded to the carbon bearing the —OH group, **914**, **944**

Tertiary amine An amine in which three H atoms of ammonia have been replaced by organic groups, 921–922, 922f, **944**

Tertiary structure, 976

Tetrahedral A term used to describe the electronic geometry around a central atom that has four electron groups. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to four atoms at the corners of a tetrahedron (AB_4), **322**

Tetrahedral electronic geometry

AB_3 species, 297–299

AB_4 species, 299–304

AB_2U_2 species, 308–310

AB_3U species, 304–308

ABU_3 species, 310

Tetrahedron (regular) A polyhedron with four equal-sized, equilateral triangular faces and four apices (corners), **322**

Theobromine, 249

Theoretical yield The maximum amount of a specified product that could be obtained from specified amounts of reactants, assuming complete consumption of the limiting reactant according to only one reaction and complete recovery of the product. Compare with Actual yield, **95**, **106**

Thermal equilibrium, 32, 33f

Thermal pollution Introduction of heated waste water into natural waters, **514**, **543**

Thermochemical equation A balanced chemical equation together with a designation of the corresponding value of ΔH_{rxn} . Sometimes used with changes in other thermodynamic quantities, **558–561**, **598**

Thermochemistry The observation, measurement, and prediction of energy changes for both physical changes and chemical reactions, **552**, **598**
bond energies, 568–571, 569t, 570f
calorimetry, 556–558, 557f
Hess’s Law, 567–568, 569
internal energy change, 571–576, 572–574f, 576–577f

relationship between ΔH and ΔE , 577–578

standard molar enthalpies of formation, 562–563, 563t

standard states and standard enthalpy changes, 561–562

thermochemical equations, 558–561

thermodynamic standard state of substance, 561–562

thermodynamic state of a system, 555

Thermodynamically favorable

(**spontaneous**) reaction A reaction that occurs with a net release of free energy, G ; a reaction for which ΔG is negative (see Section 15–16), **656**

Thermodynamic equilibrium constant The equilibrium constant defined in terms of activities of the products and reactants, **700**

Thermodynamic standard state of a substance The most stable state of the substance at one atmosphere pressure and at some specific temperature (25°C unless otherwise specified); also known as *standard state (of a substance)*, **561–562**, **598**

Thermodynamic state of a system A set of conditions that completely specifies all of the properties of the system, **555**, **598**

Thermodynamics The study of the energy transfers accompanying physical and chemical processes, **552**, 555–556, **598**

dispersal of energy and matter, 580–582, 582–583f

entropy and entropy change, 583–589, 584f, 586–587f, 588t

First Law of, 553–554, 554f

Second Law of, 589–591, 591t

spontaneity of physical and chemical changes, 578–579, 579f

Third Law of, 583

Thermonuclear energy Energy from nuclear fusion reactions, 879–881, 879f, 881f, **882**

Third Law of Thermodynamics The entropy of a hypothetical pure, perfect, crystalline substance at absolute zero temperature is zero, **583**, **598**

Thomson, J. J., 117, 120

Tin, 811

Tin chloride, 364

Titanium, 485–486

Titration A procedure in which a solution of one reactant, the titrant, is carefully added to a solution of another reactant, and the volume of titrant required for complete reaction is measured. The concentration of one solution, usually (but not necessarily) the titrant, is known; this allows one to calculate the concentration or the amount of reactant in the other, **380–382**, 381f, **393**, **772**

acid–base, **382–386**

calculation for acid–base, 382–386

calculations for redox, 390–393

Titration curve (for acid–base titration) A plot of pH *versus* volume of acid or base solution added, **765**, **772**

strong acid/strong base, 765–768, 766t, 767f, 767t

weak acid/strong base, 768–769, 769t, 770f

weak acid/weak base, 770–771, 770f

Unless otherwise noted, all content on this page is © Cengage Learning.

- Torr** A unit of pressure; the pressure that will support a column of mercury 1 mm high at 0°C, **404**, 416–418, 419, **438**
- Torricelli**, Evangelista, **403**
- Total ionic equation** An equation for a chemical reaction written to show the predominant form of all species in aqueous solution or in contact with water, **240**, 359, **367**
- Trace elements**, 1038–1039
- Trans** fats, **930**
- Transition state** A relatively high-energy state in which bonds in reactant molecules are partially broken and new ones are partially formed, **639**, **656**
- Transition state theory** A theory of reaction rates that states that reactants pass through high-energy transition states before forming products, **638**–**640**, 639–640f, **656**
- Transuranium elements** The elements with atomic numbers greater than 92 (uranium); none occur naturally and all must be prepared by nuclear bombardment of other elements, **860**, **882**
- Trigonal bipyramid** A six-sided polyhedron with five apices (corners), consisting of two pyramids sharing a common triangular base, **322**
- Trigonal bipyramidal** A term used to describe the electronic geometry around a central atom that has five electron groups. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to five atoms at the corners of a trigonal bipyramid (AB_5), **322**
- Trigonal bipyramidal electronic geometry, 310–313
- Trigonal planar (also plane triangular)**
A term used to describe the electronic geometry around a central atom that has three electron groups. Also used to describe the molecular geometry of a molecule or polyatomic ion that has one atom in the center bonded to three atoms at the corners of an equilateral triangle (AB_3), 297–299, **322**
- Triiodide, 273–274
- Triple bond** A covalent bond resulting from the sharing of six electrons (three pairs) between two atoms, 259, 259f, **280**, **319**–**320**, 319f, 320f
- Triple point** The point on a phase diagram that corresponds to the only pressure and temperature at which three phases (usually solid, liquid, and gas) of a substance can coexist at equilibrium, **474**, **495**
- Trisaccharide** A molecule consisting of three monosaccharides joined together by glycosidic bonds, **982**
- T-shaped** A term used to describe the molecular geometry of a molecule or polyatomic ion that has three atoms bonded to a central atom and two lone pairs on the central atom (AB_3U_2), **322**
- Tyndall effect** The scattering of light by colloidal particles, **535**, **543**
- Unit cell** The smallest repeating unit showing all the structural characteristics of a crystal, **495**
- Unit factor** A factor in which the numerator and denominator are expressed in different units but represent the same or equivalent amounts. Multiplying by a unit factor is the same as multiplying by one, 22–23, **35**, **53**
- Unit factor method, 22–26
- Units of measurement, 20–21, 20f, 20t, 21f, 21t
- Universal gas constant** R , the proportionality constant in the ideal gas equation, $PV = nRT$, **415**–**418**, **438**
- Universe** The system plus the surroundings, **555**, **599**
- Unpaired electrons, 161
- Unsaturated hydrocarbons** Hydrocarbons that contain double or triple carbon-carbon bonds, **890**, **944**. *see also* **Hydrocarbon**
alkenes, 899–904, 899f, 901–902f
alkynes, 905–906, 905f
- Unshared pair. see** **Lone pair**
- Uranium, 126t, 877, 877f. *see also* **Nuclear fission**
–lead dating, 868
- Valence bond (VB) theory** Assumes that covalent bonds are formed when atomic orbitals on different atoms overlap and electrons are shared, **293**–**294**, **322**
electronic geometry, 296–315
- Valence electrons** The electrons in the outermost shell of an atom, 251, **280**
- Valence shell** The outermost occupied electron shell of an atom, **288**, **322**
- Valence shell electron pair repulsion (VSEPR) theory** Assumes that valence electron pairs are arranged around the central element of a molecule or polyatomic ion so that there is maximum separation (and minimum repulsion) among electron groups, 288, **290**–**291**, 291t, **322**
electronic geometry, 295–315
- Van der Waals equation** An equation of state that extends the ideal gas law to real gases by inclusion of two empirically determined parameters, which are different for different gases, **437**, 437t, **438**
- Van der Waals forces. see** **Dispersion forces**
- Van der Waals, Johannes, 435
- Van't Hoff equation** The relationship between ΔH° for a reaction and its equilibrium constants at two different temperatures, **699**, **700**
- Van't Hoff factor (i)** A number that indicates the extent of dissociation or ionization of a solute; equal to the actual colligative property divided by the colligative property calculated assuming no ionization or dissociation, **529**, 529t, **543**
- Van Vleck, J. H., 1006
- Vapor** A gas formed by boiling or evaporation of a liquid or sublimation of a solid; a term commonly used when some of the liquid or solid remains in contact with the gas, **438**
- Vaporization**, 461. *see* **Evaporation**
- Vapor pressure** The pressure exerted by a vapor in equilibrium with its liquid or solid, **438**, **462**–**464**, 463f, 464t, 468, **495**
Raoult's Law and, 518–519f, 518–521, 521f
sublimation and, **472**, 472f
- Viscosity** The tendency of a liquid to resist flow; the inverse of its fluidity, **459**, 459f, **495**
- Visible light, 135–137, 136f
- Vitamin B₁₂, 991
- Volatile acids, 365
- Volatility** The ease with which a liquid vaporizes, 462, **495**, 519–520
- Voltage** Potential difference between two electrodes; a measure of the chemical potential for a redox reaction to occur, **843**
- Voltaic cell** An electrochemical cell in which a spontaneous (product-favored) chemical reaction produces electricity; also known as a *Galvanic cell*, **804**, **811**–**812**, 812f, **843**
construction of simple, 812–813, 813f
copper-silver, 815–816, 816f
hydrogen-oxygen fuel cell, 840–841, 841f
primary, 836–838, 837–838f
secondary, 838–841, 839f, 841f
zinc-copper, 813–814
- Volume, 21, 21f, 21t, 377
Avogadro's Law and Standard Molar, 414–415, 414t
Boyle's law and, 405–410, 408f
Charles' law and, 410–412, 411f
chemical equilibrium and, 682–683
density and, 27
First Law of Thermodynamics and, 572–574, 573f
mass-volume relationships in reactions involving gases, 426–428, 426f, 427f
specific gravity and, 29
standard molar entropy and, 586
standard temperature and pressure, 412
- Von Laue, Max, 121, 476
- Vulcanization** The process in which sulfur is added to rubber and heated to 140°C to cross-link the linear rubber polymer into a three-dimensional polymer, **939**, **944**
- Waste, nuclear, 880
- Water, 7f, 12t
autoionization of, 353–354, 364, 711–713
density, 28f
electrolysis of, 15, 15f
gases collected over, 425–426
hard, 541
heat of vaporization of, 467
heavy, 877
interfacial force microscopy, 449f
light water reactors, 876–878, 876f
purification and hemodialysis, 536–537
reactions of metal oxides with, 195
reactions of nonmetal oxides with, 195f, 197
reaction with lithium, 173f
- Wavelength (Δ)** The distance between two identical points of a wave, **134**, 135f, **163**
light, 135–137, 136f

Waxes, 887f

Weak acid An acid that ionizes only slightly in dilute aqueous solution, **210**–**211**, **211f**, **211t**, **212f**, **240**, **359**, **742f**. *see also* **Acid**
Brønsted-Lowry theory, **350**–**353**
buffering action, **756**–**758**
buffer solutions, **750**–**756**, **752t**
ionization constants for, **717**–**729**
salts of strong bases and, **733**–**736**
salts of weak bases and, **737**–**740**
titration curves, **768**–**771**, **769t**, **770f**

Weak base A molecular substance that ionizes only slightly in water to produce an alkaline (base) solution, **212**, **241**, **358**–**359**. *see also* **Base**
Brønsted-Lowry theory, **350**–**353**
buffering action, **758**–**759**
buffer solutions, **750**–**756**, **752t**
ionization constants for, **717**–**729**
salts of strong acids and, **736**–**737**
salts of weak acids and, **737**–**740**
titration curves, **770**–**771**, **770f**

Weak electrolyte A substance that conducts electricity poorly in dilute aqueous solution due to very limited ionization or dissociation, **241**, **367**
colligative property and, **529**–**530**
converting an ion to a, **795**

Weak field ligand A ligand that exerts a weak crystal or ligand field and generally forms high spin complexes with metals. A ligand that forms a weak dative bond, **1007**, **1011**

Weight A measure of the gravitational attraction of the earth for a body, **20**, **20f**, **21f**, **21t**, **35**. *see also* **Atomic weight**; **formula weight**; **molecular weight**

Werner, Alfred, **992**

Wilson, C. T. R., **861**

Windmills, **551**

Winthrop, John, **18**

Wöhler, Friedrich, **888**

Work The application of a force through a distance; for physical changes or chemical

reactions at constant external pressure, the work done on the system is $-P\Delta V$; for chemical reactions that involve gases, the work done on the system can be expressed as $-(\Delta n)RT$, **571**–**575**, **598**

Wright, Joseph, **175**, **175f**

xenon, **125f**, **416**, **1059**, **1059t**

x-rays, **117**, **121**–**122**, **122f**

diffraction, **476**–**477**

zero-order reaction, **631**–**632**

zinc-copper cell, **813**–**814**

zinc deficiency, **1038**

zinc hydroxide, **784**–**785**

zinc phosphate, **781**

zinc-SHE cell, **817**–**818**, **818f**

Zone refining A method of purifying a bar of metal by passing through an induction heater; this causes impurities to move along in the melted position, **1022**, **1023f**, **1030**

